Abschlussbericht zum Max Buchner Projekt:

Investigation of the influence of boundary layer flow on the structure of fixed biomolecules

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Introduction

For optimization of biological processes (e.g. for biological and medical applications) under shear flow the interaction between macromolecule and fluid flow have been investigated. Multi-walled carbon nanotubes (MWCNTs) are selected as model nanostructures, which have the advantage that they can be tailored for innumerable applications.

The results presented in this study are relevant for proteins and organic films (i.e. a layer of macromolecules at sub micrometer scale). Figure 1 shows a two dimensional schematic representation of macromolecules in shear flow that are attached to a substrate. This figure presents a simplified situation in which the flow field around the macromolecules influences the reaction efficiency.

The coordinate system in figure 1 shows the positive x and z-direction. The fluid flows in the positive x-direction (U) parallel to the substrate and its velocity dependents on the z-coordinate.

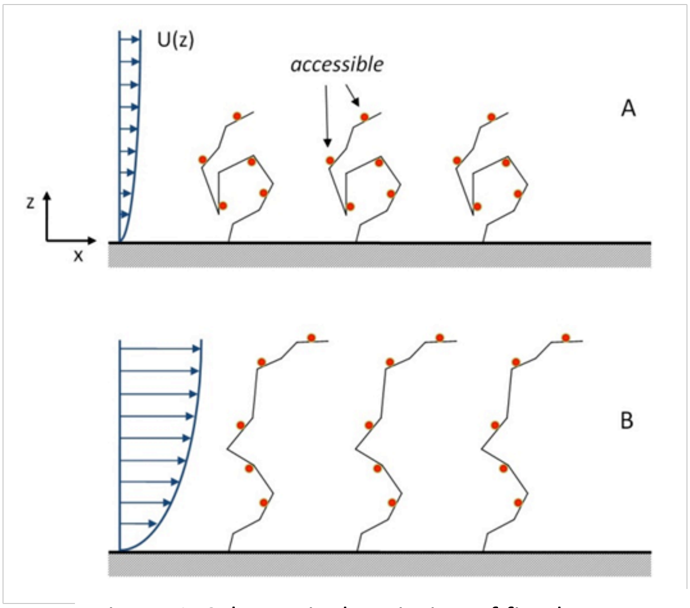

Figure 1: Schematic description of fixed macromolecules in two different velocity profiles.

Two situations are shown in figure 1 in which only the velocity profiles differ. In both situations three macromolecules are shown and each of them contains five active red centers which react with a dissolved substance. In situation A the velocity and the velocity gradient are not strong enough to "open" the macromolecule in order to give access to all the active centers; only two of five active centers are accessible.

The stronger velocity and velocity gradient in situation B enables the macromolecule to deform to its favorable open shape and gives access to all active centers.

Because investigations on the complex structure of macromolecules are difficult first measurements on well defined nanostuctures are carried out. Multi-walled carbon nanotubes (MWCNTs) are popular well defined nanostructures [1] that are used as a model nanoporous medium to study the orientation change of the MWCNTs. Moreover, nanoparticles (NPs) are filtered to demonstrate that NPs can effectively be used in future studies, in which the reaction kinetics of proteins is studied under shear flow.

Carbon nanotubes

The popularity of MWCNTs is mainly based on their extraordinary mechanical properties: four times the strength of steel, one-fifth of the density of steel and more than five times the thermal conductivity of copper for example. Because of these exceptional properties there is a wide range of applications where CNTs are used [2].
An appealing example of the popularity of MWCNTs is a device developed at the Massachusetts Institute of Technology, which can detect cancer cells in a liquid blood sample. MWCNTs form an essential part of this new device, as they work as nanoporous materials which filter the low concentrated cancer cells by an appropriate coating [3]. This is an example of chemical functionalization of MWCNTs, which can be used to prepare them for a specific task. This functionalization can be done by attaching any desired chemical species to the MWCNT in order to enhance molecular selectivity [2]

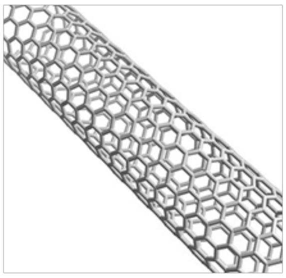

Figure 2: a SWCNT schematically presented

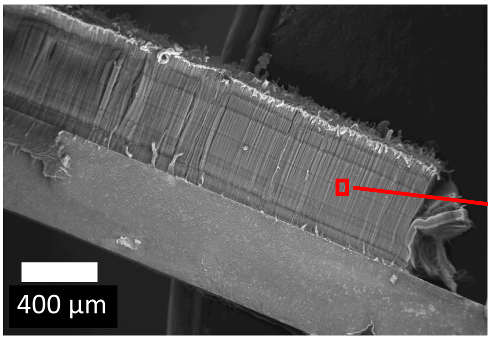

Figure 3: SEM image of the MWCNT forest.

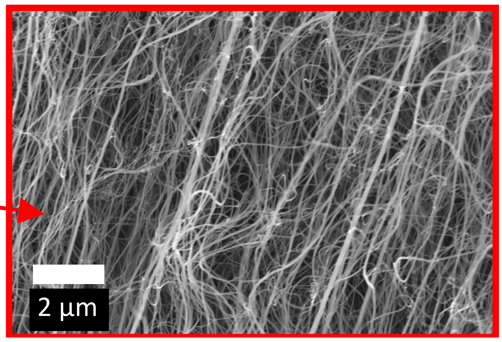

Figure 4: zoom of the MWCNT thin film.

Figure 2 shows a simplified representation of a single-walled carbon nanotube (SWCNT) with a hollow center. This SWCNT contains one cylindrical shell only. Multiple shells of SWCNTs into each other are generally known as a MWCNT. A huge number (~10^8) of close packed areas of upright standing MWCNTs on a silicon surface forms a MWCNT forest.

Figure 3 and 4 show scanning electron microscope (SEM) images of a MWCNT forest. Figure 3 shows a side view and figure 4 shows a magnification of a typical spot. These images clearly show the vertical aligned MWCNTs at larger scale, although the magnified image (figure 4) shows a more spaghetti-like morphology at smaller scale.
Based on a quantitative analysis of various SEM images the length and diameter of the MWCNTs is typically respectively 10 µm and 100 nm. The average distance between the MWCNTs is roughly 200 nm. The MWCNTs forests are produced using a conventional tube furnace aerosol-assisted chemical vapor deposition technique [4] in cooperation with the Institute of Polymer Composites (TUHH).

SEM images are the common way to get a qualitative view of the morphology of MWCNT forests. The disadvantage of SEM is that it is impossible to take SEM images of in-situ measurements, e.g. in fluid environment (under shear flow). Small-angle X-ray scattering (SAXS) on the other hand enables in-situ measurements. Microbeam small-angle X-ray scattering (µSAXS); on the other hand, is an accurate and non-destructive measurement technique.

µSAXS

µSAXS is a measurement technique where the elastically scattered X-rays are used to subtract structural information (e.g. size and shape of particles) from the sample [5]. The height and width of the incident X-ray beam typically corresponds to 20 µm x 20 µm, which leads to the term microbeam in µSAXS. µSAXS is commonly used to determine the average particle sizes, shapes and distributions. Moreover, samples measured with µSAXS can be solid, liquid or gaseous. Commonly used samples are colloids, metals, cement, polymers and pharmaceuticals, to name just a few. Only very recently µSAXS is used in fluid mechanics applications [6,7], although use of µSAXS in this field is still in its infancy. In the project presented here µSAXS has been used to study the change in orientation of the MWCNT forest under shear flow to mimic the influence of a boundary layer flow on the structure of fixed biomolecules. Furthermore, the penetration of molecules into the MWCNT forest has been measured by using nanoparticles that are detectable with µSAXS.

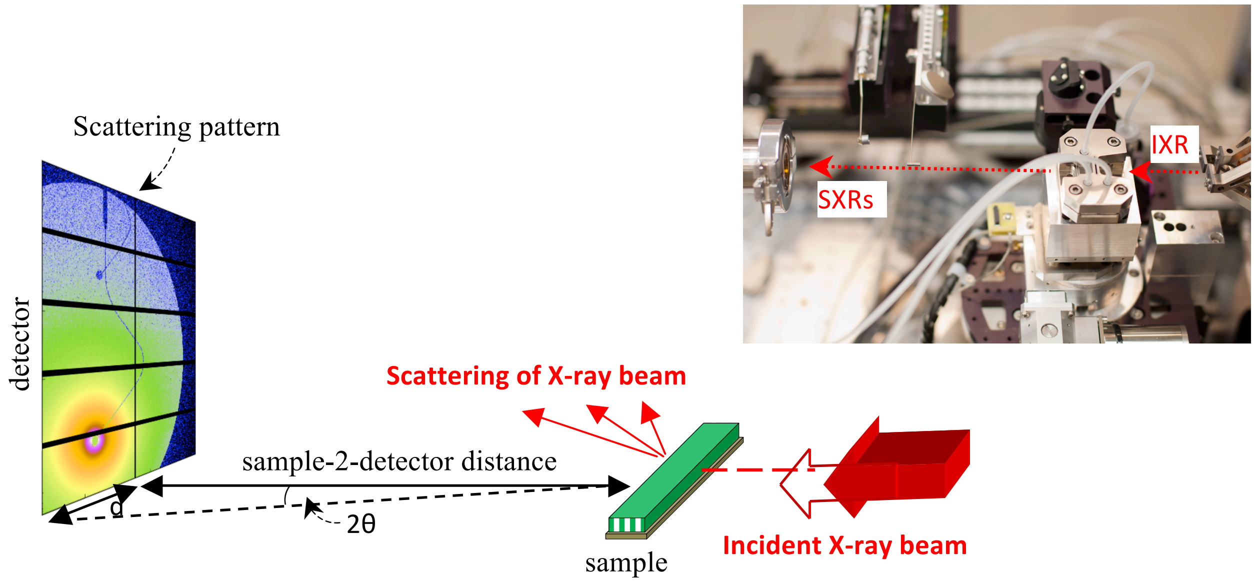

Figure 5: a conceptual explanation of µSAXS (left) and the MWCNT forest in the sample holder at the experimental station P03 (Hasylab, DESY) (top, right).

Figure 5 shows the MWCNT forest which is exposed to the incident X-ray beam. The scattering pattern at the detector, the distance between sample and the detector (SDS), half the detector distance d, the angle 2θ, the incident X-ray beam (IXR) and the scattered X-ray beam (SXRs) are all indicated in figure 5 (left). Based on the used wavelength λ, SDS, d and 2θ the scattering vector q can be determined with $q = \frac{4\pi}{\lambda}\sin(2\theta)$. The photo in figure 5 (top, right) shows the MWCNT forest mounted in the sample holder at experimental station P03 (Hasylab, DESY) [8].

Influence of boundary layer flow on the structure of MWCNT

Figure 6 presents a schematic view of the fluidic channel, in which the incident X-ray beam is scattered by the MWCNT forest. The red dot at half length and half height of the MWCNT forest represents the incoming X-ray beam. The scattered X-rays are detected by the detector, from which two scattering patterns are presented in figure 6 (right). q_x and q_y correspond to the reciprocal space (nm^{-1}) in the scattering patterns. Furthermore, the intensity bar is presented, from which is can be observed that bright colors in the scattering patterns correspond to higher scattering intensities.

The 100 µm-sized cavity between the top surface of the MWCNT forest and the roof of the fluidic channel enables a liquid (i.e. distilled water) flow both, over and through the WMCNT forest.
The viscosity of the liquid and the velocity gradient at fluid-structure interface (i.e. the top surface of the MWCNT forest) cause a shear force that can bend the MWCNT forest.

Two situations are presented in figure 6: one with a volume flux that is not strong enough to change the orientation of the MWCNT forest and one where the change in orientation is caused by the stronger volume flux. The slightly rotated WMCNT forest corresponds to a rotation of the Yoneda peak at the detector image, which is indicated by the red circle and the red arrows in figure 6 (right).

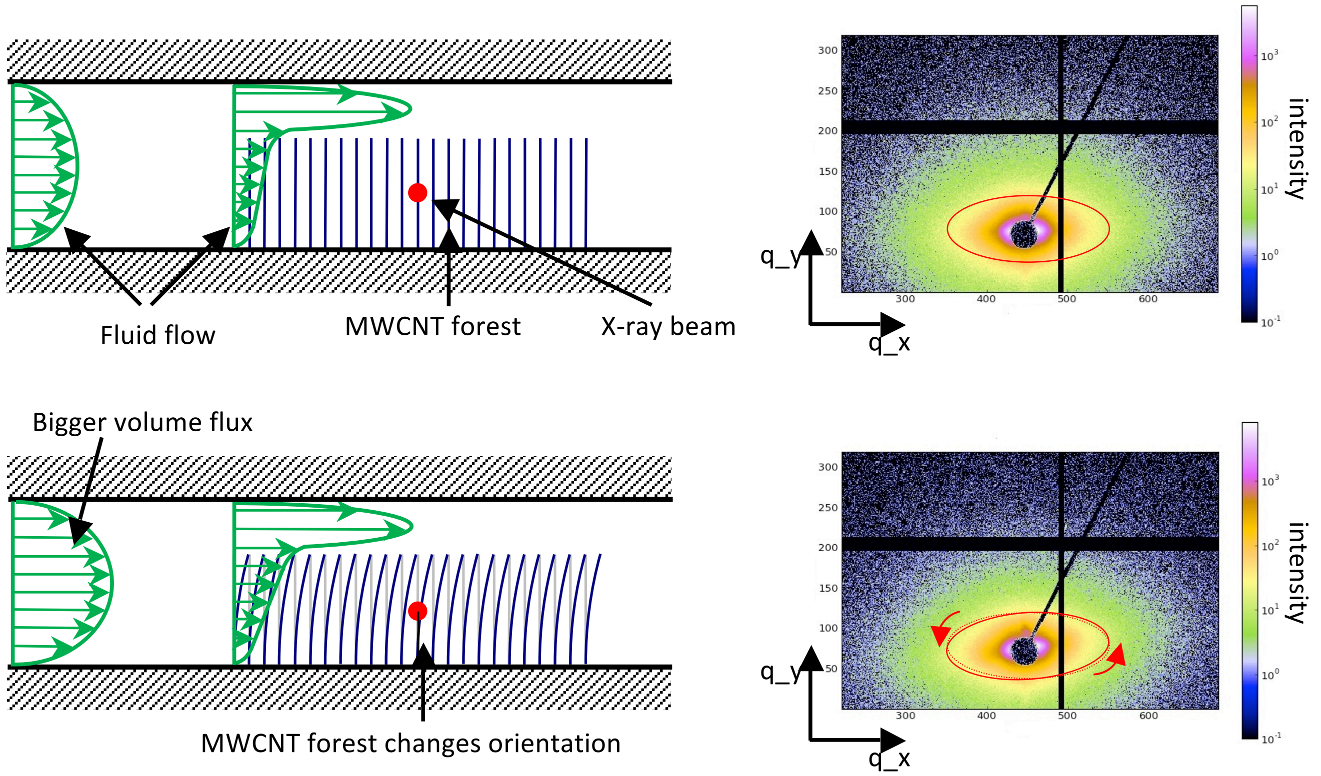

Figure 6: the MWCNT forest shown from the side; the top image shows a volume flow that is not strong enough to change the orientation of the MWCNT forest. The volume flux in the image at the bottom is big enough to change the orientation which is also observed in the scattering patterns.

This shows that a method has been developed successfully to measure the Influence of boundary layer flow on the structure of MWCNT by means of µSAXS.

Measurement of the penetration of molecules into the MWCNT forest

To measure the penetration depth of molecules into the MWCNT forest, nanoparticles have been used as tracer particles. It is shown that the penetration of nanoparticles can be detected with µSAXS. For these experiments the same experimental setup is used as presented in figure 1.

Figure 7 (left) presents a typical µSAXS image of nanoparticles that are penetrating into the MWCNT forest. The particles scatter the incoming X-rays and can therefore be detected with µSAXS. After analyzing the scattering patterns the intensity is plotted against reciprocal space (figure 7, right). The experimental observation is compared with the well-known form factor (i.e. the analytical solution) for spherical particles, which corresponds to equation 1.

$$I(q) = \left(\frac{4}{3}\pi R^3 \frac{3(\sin(qR) - qR\cos(qR))}{(qR)^3}\right)^2 \quad (1)$$

I, q and R in equation 1 correspond to the (scattered) intensity, reciprocal space and the radius of the spherical particle, respectively.

The good agreement between experimental observation and analytical solution confirms that the spherical particles are actually penetrating and subsequently detected with µSAXS. This leads to the conclusion that nanoparticles can be used as tracer particles to mimic molecules in future studies. Therefore it has been shown, that an efficient method has been developed successfully to measure the penetration depth of molecules into nanomolecular forests (like fixed biomolecules).

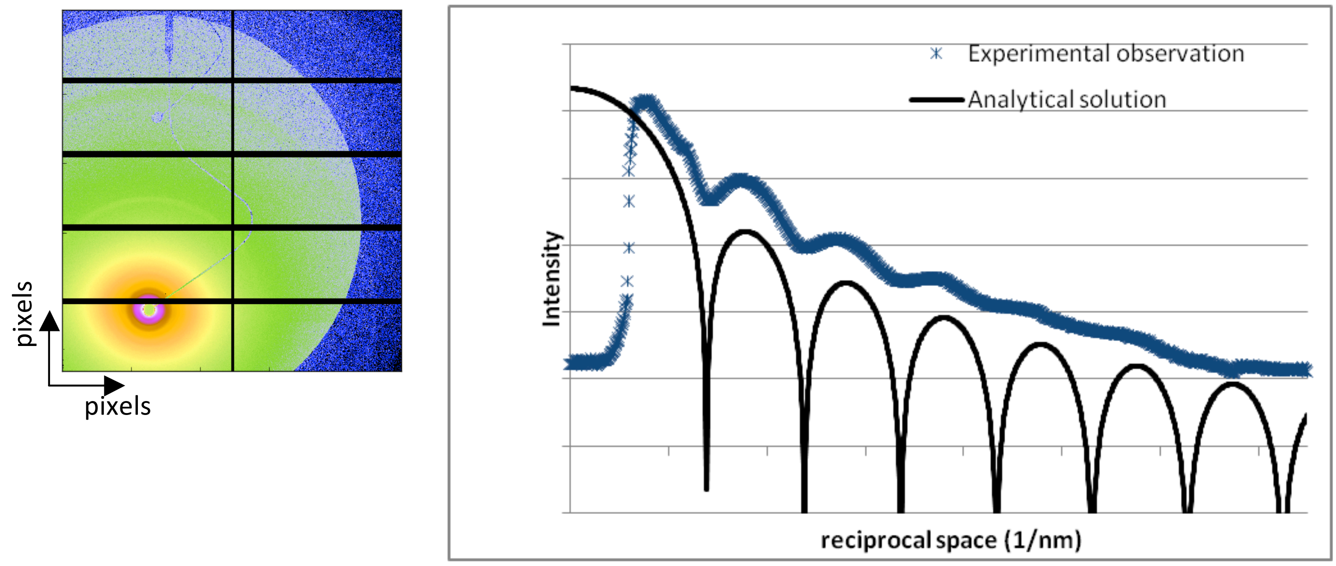

Figure 7: Nanoparticles penetrating into MWCNT forest and thereafter detected with µSAXS. A typical scattering pattern of the MWCNT forest with the nanoparticles is presented (left) and the intensity is plotted against reciprocal space after data analysis (right). The good agreement between experimental observation and analytical solution indicates that the nanoparticles can actually be detected and therefore used in future studies.

Summary

Although µSAXS is a well-known measurement technique in other fields it is not commonly used for fluid mechanical experiments. To study the complex interaction between macromolecules and liquid (solid-fluid interaction) two experiments have been carried out. In the first experiment the structure of a multi-walled carbon nanotube (MWCNT) forest, which serves as a nanoporous medium, has been changed by a boundary layer flow. This interaction has been measured by means of µSAXS measurements. Thereafter, in a separate experiment, nanoparticles have been used to study the penetration depth of molecules into a MWCNT forest. Both, orientation change and penetration depth are detected based on microbeam small-angle X-ray scattering (µSAXS), which is an accurate and non-destructive measurement technique.

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