Fingerprints of Nanostructures

Small-Angle Scattering with Neutrons (SANS)

Introduction

Small-angle neutron scattering (SANS), as as available at PSI, is an ideal tool for studying the structure of nanomaterials in the range from 1 to about 400 nm.

Imaging methods such as transmission electron microscopy (TEM) also have the capability to resolve inhomogenities on this length scale. They provide images in real space, for instance pictures of individual particles in a nanocrystalline material.

Whereas TEM is used for the visualization of single objects and the exploration of their crystalline structure, SANS is a complementary, non-destructive method providing structural information averaged over many particles of different size, with high statistical accuracy over a larger sample volume.

Small-angle X-ray scattering (SAXS) performed with modern synchrotron sources provides extremely high brilliance, and is a complementary technique to SANS.

In contrast to X-ray techniques, SANS has the advantage of being sensitive to magnetism, light elements and elements of adjacent atomic order, in particular hydrogen or deuterium that remain invisible in TEM and SAXS.

Method

During a SANS experiment, a monochromatic and collimated beam of neutrons is directed onto the sample. The resulting intensity of scattered neutrons is detected as a function of scattering angle by means of a two-dimensional ^{3}He-detector behind the sample, which can be aqueous, solid, powder or crystalline.

Applications of SANS

Typical complex material systems explored advantageously using SANS are:

- biological macromolecules: proteins, ribosomes, DNA, etc.
- polymers: molecules, chains, blends and mixtures
- surface properties of catalysts
- colloidal suspensions, surfactants
- metal physics: phase stability of alloys, precipitates, interfaces, grain boundaries
- materials science: structural tailoring and testing, stability under load
- nanocrystalline materials: grain size, interface, porosity, magnetic nanostructures
- long-range spin correlation
- magnetic flux lines in superconductors
- coating and order phenomena of magnetic fluids, ferrofluids
- location of hydrogen in large molecules

Figure 1: **Small-Angle Neutron Scattering instrument (SANS-2) at the Spallation Neutron Source SINQ.**

Examples

Medical technology:
Nanocapsules for drug delivery

Drug delivery is next to the development of the agent itself and plays an important role in the formulation of new pharmacological products. Avoidance of side effects, precise targeting of the agent and site-specific delivery into the human organism are of main concern in modern pharmaceutical research. Nano-capsules are used to supervise the release of the agent in the organism and allow for easy administration of medicaments to the patient.

TEM yields a real space image, but can not distinguish between the oil core and the polymer shell, whereas contrast variation with neutrons is able to do so. The release speed of the agent depends on the thickness and design of the polymer shell of the nanocapsule.

With contrast variation techniques using deuterated and protonated water, the thickness of the polymer shell can be determined through SANS with high accuracy, as the refraction index for neutrons of the oil, the shell and the solvent, in this case water, can be tuned. In the present example, the cores of the capsules consist of oil (Miglyol) in which the agent was dissolved. The subsequent release of the agent to the body is controlled by the thickness of the polymer shell, which also stabilizes the oil droplet inside. The agent itself is only soluble in oil and not in water, contrary to the nanocapsules, which will dissolve in an aqueous solution.

Hydrogen isotope labelling in biological science is a unique and powerful tool for neutron scattering methods such as SANS. Through variation of the refraction index of

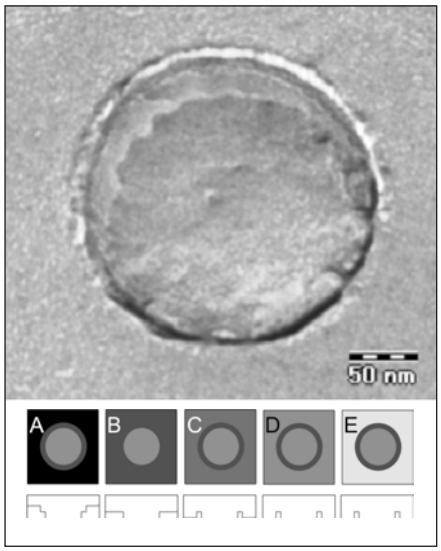

Figure 2: **Transmission Electron Microscope (TEM) picture of a nanocapsule for drug deliver.**

the solvent to the oil, only the shell remains visible (see Figure 2D) and by tuning it to the shell (Figure 2B) only the oil core remains visible. This contrast variation technique used at PSI allows imaging of the details of the inner structure of nanocapsules and hence provides structural information which is not achievable with TEM or SAXS.

Rheology – shear-induced structures investigated by SANS – flow and structural changes in liquids

Rheological properties such as viscosity, elasticity and viscoelasticity are macroscopic descriptions of a material under flow and/or deformation. Flow can induce macroscopic changes of the liquid structure. The rheological response functions reflect these changes of the sheared complex fluids. However, the direct link between the observed macroscopic rheological response and the underlying morphological changes are inconclusive and hampered by several facts:

(i) complex fluids such as suspensions, emulsions and foams, as well as molecular suspensions of surfactants, macromolecules, proteins and polysaccharides, may exhibit the same rheological response function, even though

(ii) the molecular, colloidal, and non-colloidal aggregation are controlled by different forces acting on different length scales, and

(iii) shear-induced structures appear only under shear, i.e. probing of the local microstructure under flow has to be online, should provide sufficient spatial and temporal resolution, and should probe the right length scale.

Complex fluids are subject to engineering treatment in industry (i.e. the chemical, pharmaceutical, food, and cosmetic sectors) and their quality characteristics as well as their processing behaviour are determined by their microstructure. For improved processing, it is important to access the **structure-flow relationship.**

An inherent problem in rheological research is the fact that shear-induced structures cannot be investigated at rest using microscopes or other imaging techniques. The combination of a sophisticated rheometer with SANS techniques at PSI provides the experimental basis for investigating complex rheological flow behaviour and its microstructural origin, in particular when focusing on the time evolution and transient coupling of microstructural and macroscopic rheological properties, providing the missing link between flow and structure.

Structural changes in surfactants

In collaboration with the Institute of Food Science and Nutrition at ETH Zurich, PSI has investigated in surfactants the formation of alternating shear bands in a wormlike micellar solution, in terms of both temporal and spatial oscillations.

Figure 3: **Installation of a standard rheometer on the SANS-1 instrument to study the molecular structure and the rheological properties of a liquid.**

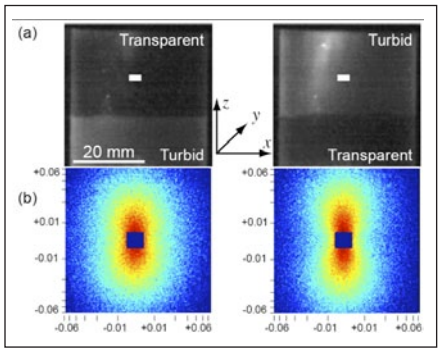

Figure 4: **Shear bands in a Couette-type rheometer at a time difference of 1 second, showing that the turbid band is changed into a transparent one and vice versa. The corresponding SANS patterns from the area of the white bar are shown below the pictures.**

Figure 4a shows the transparent and turbid shear bands in the shear cell at a time difference of one second.

A flip-flop motion of the bands could be identified. Figure 4b shows the corresponding two-dimensional scattering patterns obtained by synchronizing optical appearance of the band and neutron detection. Here, fast acquisition and the synchronization of both the rheological and scattering data are crucial for further understanding of the coupled flow-structure feedback. The scattering pattern gives detailed information about the degree of alignment of the molecules and structures in the solution, as well as about the structure and sizes.

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