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Particle shape effects in colloidal crystals and colloidal liquid crystals: Small-angle X-ray scattering studies with microradian resolution

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ABSTRACT

Small-angle X-ray scattering (SAXS) is an indispensable tool in structural investigations of self-assembled colloidal crystals and colloidal liquid crystals. This paper reviews recent studies of the particle shape effects on the crystal structure as revealed by SAXS. Rod-like, plate-like, biaxial board-like as well as cubic-like shapes are discussed. Since relatively large, (sub)micron particles are often used in these studies, we describe the principles of the microradian X-ray diffraction technique that allows detailed characterisation of the periodic order including the determination of the intrinsic width of the Bragg peaks.

1. Introduction

Structures on the mesoscales, ranging from about a nanometre to a micron, play a key role in a broad range of research fields such as soft matter [1,2], heterogeneous catalysis [3] and biology [4,5]. They can be studied either in direct-space using microscopy or in reciprocal-space using scattering that are complementary to each other.

Microscopy data is more straightforward and can usually be interpreted in an easier way. However, it yields information on small sample volumes the choice of which is often biased by the observer. Electron microscopy is very powerful as it can access all scales of interest down to the atomic scale. However, this technique is limited in accessing bulk structures and is not suitable for in-situ and time-resolved studies. The latter can be solved using optical microscopy but only on large scales. Recent developments of super-resolution optical microscopy techniques [6] are a great step forward but they are applicable only to systems that can be labelled with fluorescent dyes.

In contrast, scattering techniques are able to provide mesoscopic structural data averaged over macroscopic volumes. They are often perfectly suitable for in-situ and time-resolved studies in the bulk. Light scattering is easily affordable but only provides access to a very limited range of q-values and often suffers from multiple scattering. Small-angle neutron scattering (SANS) has a number of important advantages such as contrast variation possibilities and sensitivity to magnetic structures. However, low brightness of neutron sources limits the range of applications of SANS. Nowadays small-angle X-ray scattering (SAXS) is widely recognised as an indispensable structure characterisation tool at the mesoscopic scales. Recent developments of synchrotron sources and X-ray detectors provide a very fast and effective tool to study colloidal crystals and their real-time development. The high penetration power of X-rays makes SAXS applicable to almost all system types. In addition, the intrinsically low contrast of all materials for X-rays ensures, in the vast majority of cases, a high quality of the scattering data that is free of multiple scattering contributions. SAXS also gives access to a broad range of spatial scales from a nanometre to microns. Moreover, as we shall discuss in more detail below, positional correlations on distances up to submillimetre can be accessed from the width of diffraction peaks measured with microradian resolution.

In this review we shall focus our attention onto the recent studies of crystals and liquid crystals obtained by the self-assembly of colloidal particles. Their self-assembly can be directed in various ways, for instance by applying an external electric or magnetic field [7,8]. Alternatively, one can vary the particle shape to achieve novel colloidal lattices [9–11]. The use of strongly anisotropic shapes leads to a very rich phase behaviour including numerous liquid-crystalline states, which are of interest for researchers and engineers to prepare new nanomaterials with novel symmetries using self-assembly techniques. Their crystal structures, however, have to be carefully characterised in order to be employed as such and this is where SAXS analysis plays an important role.

The rest of this review is organised as follows. Section 2 is devoted to the discussion of how to achieve microradian resolution in SAXS

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experiments. Section 3 provides a short summary of the form factor scattering that can be measured in dilute suspensions. This is followed by an overview of the recent developments in the studies of liquid crystals formed by rod-like, plate-like and board-like colloids in Section 4. In this part the behaviour of these anisotropic particles in external magnetic fields is also reviewed. In Section 5, we describe the investigations of structures formed by cubic-like colloids which have been performed in the last few years. Finally, a short summary is given in Section 6.

2. Microradian X-ray diffraction

Application of X-ray scattering to study the self-assembly of large, (sub)micron-sized colloids is challenging due to the enormous, 3 to 4 orders of magnitude, difference between the scale of interest and the X-ray wavelength λ that results in very small diffraction angles, $2\theta \sim \lambda/d \sim 1 \ldots 0.1$ mrad, where d is the period of the structure. To resolve such diffraction patterns, one needs to have a resolution significantly better than these values of 2θ. Moreover, very useful information is contained in the width of the diffraction peaks, which sets the resolution demands much higher.

For example, in a perfect but small crystal the peak width is determined by the inverse crystal size. This finite-size broadening is the same for all diffraction peaks but can depend on the direction in 3D reciprocal space for crystals with anisotropic shape. The broadening is the strongest in the direction of the smallest crystal size (e.g., along the normal for a thin crystalline film). Moreover, diffraction peaks can be broadened by defects and strain fields, which deform the ideal crystal lattice. This "second-type disorder" in the terminology of Guinier [12] leads to peak broadening that depends on the q-value. Since in small-angle X-ray scattering experiments multiple diffraction orders can often be simultaneously measured, it is straightforward to apply the Willamson–Hall analysis to colloidal crystals [13], which allows one to determine the typical crystal size and the strength of the strain field.

To illustrate what type of information can be revealed by SAXS, we show in Fig. 1 two examples of 2D patterns measured with microradian resolution using different crystals of colloidal spheres [14,15]. There are strong similarities between the patterns and the data may have looked nearly identical if measured with a lower resolution. However, thanks to the microradian resolution, one can now see a striking difference in the width of the reflections. In Fig. 1a one can also see that the peak broadening can be anisotropic. The width δq_r in the radial direction is the measure of the spatial extent of the periodic order and the strain. The width of the peak δq_ϕ in the orthogonal azimuthal direction can possess additional contributions originating from fluctuations of the exact orientation of the crystallographic axes within the irradiated area of the sample. In the latter case the reflections often possess an arc-like shape. Moreover, crystal imperfections can lead to additional scattering in between the Bragg peaks, which can also bring useful structural information on the colloidal structures.

To summarise, small-angle X-ray diffraction is able to provide a wealth of information about the periodic order and imperfections in colloidal crystals, just similar to X-ray diffraction (XRD) in ordinary, atomic or molecular, crystals. To obtain this information is, however, challenging, especially for crystals made of large (sub)micron particles. Ideally, one would need to achieve resolution in reciprocal space corresponding to submillimetre direct-space distances to be able to probe positional correlations on a distance of the order of hundred lattice periods. For X-rays with the wavelength of $\lambda \sim 0.1$ nm, the angular resolution of the order of a microradian is therefore required.

How can one actually achieve the microradian resolution in small-angle X-ray scattering experiments? Does one need to build a very long beamline with extremely large sample-detector distance as in Ref. [16]? Does one need to use a "pencil-beam", *i.e.* a very thin X-ray beam? Or, does one need instead to strive for achieving a very parallel beam? To correctly answer these questions, we need to recall that X-ray scattering is essentially a coherent process. To be able to achieve a reciprocal-space resolution of δq, one has to make sure that waves scattered at points separated by a distance of the order of $2\pi/\delta q$ are still able to interfere at the detector. It is therefore important to consider the beam coherence.

2.1. Transverse coherence and angular resolution

Transverse coherence is related to the finite size of the X-ray source, the electron beam in the synchrotron in our case. Random summation of waves emitted at different points of the incoherent source leads to random modulation of the phase of the X-ray wave in the transverse direction [17]. The transverse coherence length l_{tr} is defined as the distance along a wave front over which the phase fluctuations become significant. As a result, the interference of waves scattered by particles separated by more than l_{tr} vanishes after averaging over all random realisations. For a freely propagating X-ray wave the transverse coherence length $l_{tr} = L\lambda/(2d)$ [17] is determined by the source-sample distance L, the X-ray wavelength λ and the transverse source size d. By using typical values of $L \sim 50$ m, $\lambda \sim 0.1$ nm and $d \sim 0.1 \ldots 1$ mm, one can estimate $l_{tr} \sim 2.5 \ldots 25$ μm. This means that the existing synchrotron sources have the potential of probing positional correlations on distances up to a few microns or even tens of microns. With the current upgrade plans of the modern synchrotrons such as the ESRF [18], even submillimetre values of l_{tr} can become feasible.

Fig. 2 shows a few illustrations of the possible SAXS setup schemes that can be used. Double-headed vertical arrows denote refractive

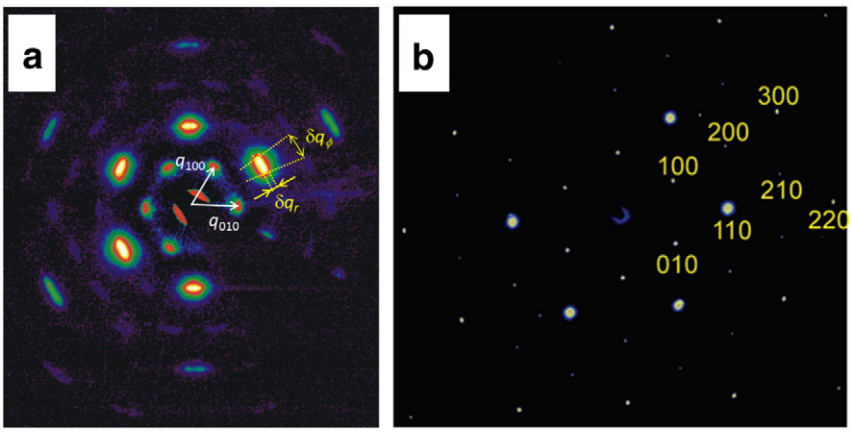

Fig. 1. Examples of the small-angle diffraction patterns measured with an angular resolution better than 10 μrad. The pattern in (a) is measured from a colloidal crystal of 425 nm polystyrene microspheres grown on a glass substrate using the vertical deposition technique [14]. The pattern in (b) is obtained from a sedimentary crystal of 224 nm silica spheres [15]. The intense diffraction peaks of the 110 family in panel (b) strongly saturate the detector and their apparent width is exaggerated.