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Topical Review

Past, present and future—sample environments for materials research studies in scattering and spectroscopy; a UK perspective

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Abstract

Small angle x-ray scattering and x-ray absorption fine structure are two techniques that have been employed at synchrotron sources ever since their inception. Over the course of the development of the techniques, the introduction of sample environments for added value experiments has grown dramatically. This article reviews past successes, current developments and an exploration of future possibilities for these two x-ray techniques with an emphasis on the developments in the United Kingdom between 1980–2020.

Keywords: SAXS, XAFS, sample environment, soft matter, materials science

(Some figures may appear in colour only in the online journal)

1. Introduction

It is remarkable how x-ray based research on materials science has changed over the last 30 years. Where 30 years ago many diffraction experiments still used x-ray film as the main detection method there is now a plethora of highly efficient electronic detectors available that can collect and store large data volumes in fractions of a second (Broennimann et al 2006). Some are even pushing the limit further (Dinapoli et al 2013, Mozzanica et al 2018, Martiel et al 2020). At the same time developments in x-ray generators, especially when synchrotron radiation (SR) storage rings are included, have allowed for ever more bright and brilliant x-ray bundles (Bilderback et al 2005, Weckert 2015). The improvement in x-ray optics has also been considerable: when the number of photons per unit cross section is measured, one can see that...
the achievable brilliance increases on SR beamlines even surpasses the well-known Moore’s law which is so popular in the semi-conductor industry.

The increase in raw flux, in combination with improvements in detector technology, has allowed a paradigm shift from static structural determinations to time-resolved experiments where structural changes and reaction kinetics can be followed in real time. With this shift has come an increased interest in the development of sample environments and other instrumentation required to obtain relevant information. Increased control over the sample can raise an experiment to the level that it allows one to understand the physical and chemical events in, for instance, an industrial manufacturing process (Portale et al 2013) or the duty cycle of an artificial heart valve (Stasiak et al 2011).

X-ray spectroscopy and x-ray scattering are two classes of techniques that have greatly benefited from the technological developments and have consequently become workhorses for materials science research.

Although above we mention separate reasons for advances, in fact no single reason sparked these developments and the curiosity and inventiveness of groups of collaborating individual researchers and engineers, in combination with many hours of overtime, is certainly not the least important contributory factor. In the end it comes down to ‘the ability to get things done’ is a combination of two elements: the desire to do them and the capacity to triumph over the challenges associated with doing things that are difficult (James 1980).

We will briefly describe some of the historical developments and science that had been made in the first facility in the United Kingdom, specifically designed for the generation of SR, to become operational as a user facility and how this has progressed to the modern day.

2. Driving factors early days

The advent of dedicated storage ring beamlines (Dobson et al 1986, Kuroda 1989, Derbyshire et al 1989, Bark et al 1990, Bras et al 1993, Bilsborrow et al 1995, Latimer et al 2005), with high flux, in the 1980’s and 1990’s allowed the materials science community to start to think in terms of the real science problems they were engaged in. The opportunities to answer these scientific questions including ‘how does a material behave in time when perturbed physically or chemically?’ And ‘what can we learn from that to improve the materials?’ The development of a combination of simultaneous technique combinations and new sample environments led by, among others, people such as Greaves in Daresbury and Zachmann in Hamburg.

One of the most often used materials science characterization techniques is x-ray powder diffraction. Time- or temperature-resolved experiments were already implemented on laboratory x-ray generators but non static experiments with a reasonable time-resolution so that chemical and physical transformations could be followed, came completely of age on the first SR beamlines. Here the broad x-ray spectrum could be used to carry out energy dispersive x-ray diffraction experiments (Clark 1996). Apart from the time resolution that this technique could bring, a second advantage was that only a small beam access opening in the sample environment had to be created. This in contrast with angle dispersive experiments where a large opening angle is required. This simplified the engineering issues and enabled high temperature and pressure experiments suitable for catalysis research. At the SRS (Martin 1988) (Synchrotron Radiation Source) in Daresbury this also led to the installation of a powerful multi anvil press suitable for large sample volumes (Clark 1996). In the early years this instrument was mainly used to gain insights in the transformations, and possible structural intermediates, in geological compounds (Yee et al 2006, Hunger and Benning 2007). In later years this technique was also used to observe the pressure induced formation of materials that could compete with diamond in hardness. On a modern synchrotron this technique has lost some of its appeal due to the very high fluxes to which the sample is exposed, and the use nowadays is mainly limited to experiments that are short and require a very high time-resolution (Bourgeois et al 2003). In the meantime, the angle dispersive techniques have become so advanced by the introduction of position sensitive or multiple point detectors that time resolved experiments have become routine as well (Tabatabaei et al 2009).

These sorts of questions were a paradigm shifts away from obtaining structural data for pure knowledge’s sake but needed a whole new infrastructure to achieve them. The advent of detectors designed to cope with the flux levels in x-ray scattering experiments (Gabriel 1977, Bordas et al 1980) at these new facilities allowed this infrastructure to develop into the time-resolved experiments that are ubiquitous today. EXAFS studies of dilute systems were originally only possible at low count rates using photomultiplier tubes as detectors of the fluorescent x-rays (Hasnain et al 1984). The improvements in fluorescence detection of dilute components in a sample were the result of putting together a large number of elements on a single cryogenically cooled detector head (Cramer et al 1988), but the advent of multi-element, 30 and ultimately 100, solid state germanium detectors and improved processing electronics (Derbyshire et al 1992, Farrow et al 1998) allowed experimenters to make full use of available flux. A special development was the nine-element monolithic Ge detector developed by Canberra and using the Daresbury developed electronics. The monolithic design allowed a larger solid angle to be covered compared to single element type of detectors and a much more efficient use of the active area of the detector since no photons were lost in the space between individual elements (Derbyshire et al 1999). Not only were the detectors important, but to record time-dependent x-ray spectroscopic measurements, it was necessary to be able to record a spectrum in a time much faster than the typical ~1h recording times of early facilities. New monochromators were developed which could record a complete spectrum in only a few seconds in a technique that became known as quick EXAFS, or QuEXAFS (Frahm 1989, Frahm 1991, Murphy et al 1995). The first low-profile monolithic Ge detector when combined with digital readout electronics such as XPRESS (Farrow et al 1995) allowed data to be collected rapidly from sub 1% dilutions (figure 1).
One of the earliest examples of a kinetic study in small angle x-ray scattering (SAXS) was where temperature was used to explore the behaviour of polymeric material by Koch et al (Koch et al 1979). They followed the crystallisation process of pre-stretched polysisobutylene fibres, finding that the half-time for the crystallisation was approximately 50 seconds. Zachmann and co-workers (Elsner et al 1981) studied the evolution of SAXS from amorphous poly(ethylene terephthalate), (PET), during isothermal crystallization using SR. Data was recorded in 1 sec intervals while the samples were heated to temperatures between 117 °C and 145 °C to explore the kinetics of the process.

A crucial driving force was the concept that, to understand evolving samples, required one to obtain information over several decades in length scales, which consequently called for the combination of several experimental techniques in a single experiment. This led to parallel developments of combined SAXS/WAXS beamlines in Hamburg and Daresbury (Bark et al 1992, Bras et al 1993), indicating that both the time and technology were ready for such developments. Preceding structure formation, in for instance zeolite formation, chemical reactions are taking place which can be elucidated by x-ray spectroscopy (Gottler et al 1989, Clausen et al 1993). The subsequent crystallization process requires a combination of small and wide-angle x-ray scattering, where initial signatures from phase separation come from larger length scales accessible by SAXS and the ultimate crystallisation kinetics require time resolved WAXS (Beelen et al 1993, Dokter et al 1995). Early attempts to record fast WAXS results were limited by the technology: the only system capable of recording a complete WAXS spectrum without moving the detectors was the INEL streamer discharge detector (Evain et al 1993), but its maximum count rate was only a few kHz: building on technology developed for high energy physics experiment, gas microstrip (Zhukov et al 1997, Bateman et al 2002) detectors were used which were up to 500 times faster. The WAXS data was also collected using the RAPID multiwire proportional counter (Lewis et al 1997a) which was capable of recording at a global rate of 200 MHz (figure 2).

An area where combining SAXS with WAXS was crucial was in the crystallisation of cordierite glass ceramics (Bras et al 2005, Bras et al 2009). This material, because of its low average thermal expansion coefficient, high thermal shock resistance, excellent chemical stability, low dielectric constant and optical transparency was of significant interest to the automotive industry as the honeycomb support for exhaust catalysts but also for substrates in electronic packaging and in the development of tunable lasers and solar concentrators. Independent studies could not give the whole picture, whereas the newly arrived combined SAXS/WAXS capability on 8.2, instigated by Greaves et al, unambiguously showed the crystallization pathway. Studies to explore crystallisation in homopolymers (Ryan et al 1994) and phase behaviour in block copolymers (Forster et al 1994, Khandpur et al 1995) soon followed. This seminal work on block copolymers is still being cited today. Combined SAXS/WAXS beamlines are now the norm for materials science studies which makes it impossible to give a comprehensive list (Riekel et al 1996, Kellermann et al 1997, Bras et al 2003, Cernik et al 2004, Krywka et al 2007, Hexemer et al 2010, Weigand and Keane 2011, Buffet et al 2012, Kirby et al 2013, Smith et al 2021).

The development of time-resolved methods also required an increased control over, for instance temperature, which was most often the parameter driving the reaction or crystallisation kinetics. Subsequently many novel homemade devices (Fan et al 2007, Sankar 2007, Sankar et al 2007) as well as more commercially driven solutions such as the Linkam hot-stages (Oversluizen et al 1995, Bras et al 2005) and DSC cells (Russell and Koberstein 1985, Kellens et al 1991, Bras et al 1995a) were introduced to further improve temperature control; the latter providing additional chemical information in the form of glass transition temperature, melting and crystallisation points. As with many scientific advances they rarely stay unique to the field that developed them. Temperature control was soon exploited to explore the structure of the lipid channels in human skin (Bouwstra et al 1996) relevant for transdermal drug delivery and later also for understanding of skin diseases like eczema and psoriasis (Janssens et al 2012). Soon many fields were exploiting the techniques developed including food science where the development of starch structure during cooking was explored (Jenkins et al 1994).

For even more accurate temperature control Peltier devices were deemed necessary for some investigations. An exploration of undercooled water (Dings et al 1992) required 4 Peltier units surrounding the sample but gave the investigators 0.05 °C gradients to work with.

The desire to be able to perform time-resolved and combinations of techniques was also felt in the x-ray spectroscopy community. Greaves in Daresbury became one of the most ardent advocates of these developments. Initially experiments were performed by the energy dispersive EXAFS (EDE) community, where the first dedicated diode array detector system for collecting data was developed at Daresbury by Allinson et al (Allinson et al 1988). In the early days, Hamburg was also developing the technique and the first combined EDE/XRD experiments (Clausen et al 1993) were carried out there by measuring the diffraction from an individual peak. The first combined experiments at Daresbury on beamline 7.4 followed measuring the structural and chemical changes that occur within the layered mineral aurichalchite (Cu5−xZnx(OH)6(CO3)2) when heated in dry air to approximately 450 °C. This experiment showed the value of combining the techniques and including temperature control (Couves et al 1991).

Quick EXAFS (QuEXAFS), by using scanning monochromators instead of energy dispersive methods, soon followed and gave the opportunity for improved data quality the required time resolution (Frahm et al 1995, Murphy et al 1995). Once available the technique showed its value in a range of scientific areas including zeolites (Sankar et al 1993, Thomas et al 1994) and the field for which Greaves is most remembered, random network glass (Houde-Walter et al 1993). Dedicated sample environments soon followed (Dent et al 1995) again, influenced by the need to study inorganic materials in operating conditions (Thomas et al 1995). For a further
improvement in the possible time resolution, one had to wait until the advent of the third generation of synchrotron sources (Grunwaldt et al 2001, Lützenkirchen-Hecht et al 2001).

If the combination of other x-ray based techniques is an obvious development, the addition of non-x-ray based techniques broaden the possibilities to increase the information content of an experiment but often at the expense of a more complicated protocol, where for instance access by two different type of probe beams has to be enabled. This was already clear in the development of on-line DSC, where the normal thermal isolation of the sample has to be breached in order to allow access with the x-ray beam. It is even more so when optical access to the sample has to be allowed. An example where birefringence was combined with x-ray scattering shows the ingenuity which was required to achieve this (Gleeson et al 1995), but also the benefits of having the possibility to correlate the macroscopic behaviour with events at the molecular level for liquid crystals subjected to changing electric field.

For spectroscopy at different wavelength ranges one can encounter issues with discrepancies in penetration depth and sample environment window transparency, but the promise of a more complete insight in the processes under consideration drove many researchers to team up with beamline scientists in attempts to overcome these issues. Sometimes the data quality was maybe not optimal, but acceptable and of sufficient quality to be analysed, instead of remaining stuck at the proof of principle level.

2.1. SAXS/WAXS/chemical spectroscopy

Combining SAXS/WAXS/Raman spectroscopy allowed chemical reaction kinetics to be established alongside any structural changes. Bryant et al used this to good effect in the polymerisation reaction of styrene into polystyrene (Bryant et al 1998). Raman spectroscopy can be realised through the application of fibre optics and is therefore highly versatile and has been successfully combined with XRD/EXAFS (Kongmark et al 2009) and SAXS/WAXS/EXAFS (Beale et al 2011) and is now utilised widely, including for determining the ratio of bundled to isolated carbon nanotubes. Without the Raman spectroscopy data this would be an ill-posed problem, whereas its inclusion allows one to apply the appropriate constraints in the modelling of the SAXS data (Haas et al 2014). Davies et al incorporated microRaman spectroscopy (Davies et al 2009) with microdiffraction onto ID13 (Engström et al 1995) at the ESRF. The combined technique was used to study the sol–gel synthesis of silica in an ionic liquid (Nayeri et al 2015). Even more recently Raman spectroscopy has been combined with SAXS to explore the ozonolysis of oleic acid-sodium oleate cooking aerosol proxies (Milsom et al 2020, Milsom et al 2021). Similar developments were attempted with infra-red spectroscopy but despite the promise of this approach it never developed a widespread following (Bogg et al 1995, Bras et al 1995b).

2.2. Exploitation for polymer processing

During materials processing, mechanical performance as well as determining lifetime of components it is relevant to understand what the reaction of the materials is when exposed to mechanical forces. This can be in the liquid state where an inevitable step in the processing of polymers is to be exposed to shear forces or the ultimate breaking strength of fibres intended to be used in composite materials.

Although high on the list of polymer scientists, the use of shear devices or rheometers in the early years was not widespread (Pople et al 1998, Mitchell et al 1998, Hamley et al 1998). One of the reasons was that these devices would benefit from a somewhat higher penetration power. This was not available on the fixed energy beamlines which were mainly tuned to the traditionally available Cu Kα wavelength. Some interesting work was carried out using a multipass rheometer that followed the evolution of crystallisation, as molten polyethylene flows into a slit geometry (Mackley et al 2000). However, home built or modified commercial stretching devices were introduced to the beamlines for the study of polymers (Blundell et al 1994, Butler et al 1995, Streebuck et al 1997). Even biaxial deformation has become possible (Gurun et al 2009). It should be mentioned that for these studies the data analysis was still primitive due to a lack of computational power. Elaborate attempts to remedy this were undertaken (Streebuck et al 1997) but to access all the available information that was embedded in these experiments had to wait until computing power caught up with the data volume.

These developments led to new questions which required higher brightness to solve. Experiments by Ryan et al (Terry et al 1998), using an on-line polymer extruder on 16.1 at Daresbury (Bliss et al 1995) and elsewhere (Miyata et al 1997), reignited the debate about the onset of polymer crystallisation (Schultz et al 2000). The common wisdom at that time was that this was a nucleation and growth process but combined SAXS/WAXS data showed the existence of a mesophase before the onset of crystallization (Olmsted et al 1998). This caused some heated debates in the polymer crystallisation community (Heeley et al 2003). The accepted outcome of this debate is that indeed a mesophase appears before crystallisation starts.

3. Modern beamlines and combined exploitation

3.1. SAXS

The sample environment types described above are still the workhorses for much of the productivity of SAXS beamlines globally today. For example, the Linkam DSC is still used for continuing work on studying hybrid glasses from metal organic framework liquids (Bennett et al 2015).

The use of pressure in soft materials research has more recently become well established. A number of cells have been designed which match the requirements of soft matter (Duesing et al 1996, Kato and Fujisawa 1998, Steinhardt et al 1999, Woencnhaus et al 2000, Ando et al 2008, Krywka et al 2008). These allow the experimenter to vary the pressure and measure morphological properties of the material of interest. More recently kinetics has started to be considered, pressure may well be a cleaner medium to understand phase transitions than temperature. A P-Jump cell developed by Brooks et al...
(Brooks et al 2010) has been extensively used in soft mater studies (Brooks et al 2011, Tang et al 2012, Tyrsted et al 2012, Barriga et al 2015, Schroer et al 2016, Schroer et al 2018, Le Vay et al 2020) on I22 at diamond.

The study of reaction kinetics is also fairly common, even under environmental science conditions (Stawski et al 2020), as is the use of bespoke reaction cells for monitoring reaction progress (Brotherton et al 2019, Alauhdin et al 2019). Flow cells and the associated stop flow technique (Grillo 2009) has also been used extensively in soft matter research. As long as the research team has enough material this can be a good way of accessing very fast timescales indeed (Graceffa et al 2013). Microwave annealing (Toolan et al 2017) has also been utilised as an alternative to thermal annealing for optimising block copolymer self-assembly by targeted annealing of specific regions of a multi-component system. Opening routes for the development of ‘smart’ manufacturing methodologies. Online chemistry, following the structure formed by chemical reactions, also have become feasible even when using high pressure equipment like super critical CO2 chemistry cells (Hermida-Merino et al 2014), On-line chemical installations to drive structural deformations in block co-polymers, mimicking the behaviour of muscle, have also been reported (Howse et al 2006).

Evermore complex sample environments mimicking real world processing conditions have been exploited, even in grazing incidence mode (Proller et al 2017), an excellent review of those used in polymer science has recently been written (Portale et al 2016).

To obtain very high temperatures, well beyond those developed for early thermal studies, alternative solutions have been explored. These include aerodynamic levitation laser heating (Hennet et al 2011) for which study of molten glass (Hennet et al 2007, Greaves et al 2008, Greaves et al 2009) was of particular note. The beauty of this method is that the sample is suspended without need for sample holder simplifying any background subtraction and allows for the integration of additional techniques. An excellent recent review discussing these sample levitation developments in several international x-ray and neutron sources is published by Benmore and Weber (Benmore and Weber 2017).

With the reduced beam sizes and lower divergencies associated with modern SAXS beamlines, microfocus studies have expanded dramatically. While many are associated with mapping (Hermes et al 2006, Seidel et al 2008) microfluidic devices which have been developed in most of the soft matter fields (Barrett et al 2006, Kadiak et al 2017, Hashemi et al 2019, O’Connell et al 2019) are already being exploited to study flow (Martin et al 2016, Lutz-Bueno et al 2016, Levenstein et al 2019) and rheological properties of soft mater (Komorowski et al 2020, Dinic et al 2017).

Improvements in beam quality allowed grazing incidence SAXS/WAXS to become mainstream, indeed it is the mainstay of the science programme on MINAXS (Buffet et al 2012) at Petra III. Early experiments at the ESRF on ID13 (Engström et al 1995) showed that position-sensitive sample surface information of multiple-scaled polymer films (Müller-Buschbaum et al 2003) was possible with micro-focused beams from 3rd generation facilities. An excellent review of what is currently possible can be found in the review article by Hexemer et al (Hexemer and Müller-Buschbaum 2015).

Sample environments have developed in this field too from fairly rudimentary heated cells (Carmichael et al 2001) to very elaborate systems that can sputter new layers of gold in situ (Roth et al 2006, Al-Hussein et al 2013, Schwartzkopf et al 2013), even showing that such complicated systems are ‘portable’ (Dohrmann et al 2013, Roth et al 2015)
some instances, or even follow the evolution of structure via laser/surface modification (Rebollar et al. 2015). Others have used the slot-die printing (Proller et al. 2016) or doctor blade formation (Pineda De La O et al. 2021) of thin films in situ to gain a fuller understanding of the evolution in structure in photovoltaic devices. Understanding the preparation of poly(3-hexylthiophene) (P3HT), used in some of these organic photovoltaic devices, has been studied by x-ray absorption fine structure (XAFS). It was widely thought that FeCl$_3$ acted as an oxidant. A study by Hirai et al., however, showed that the generated Fe(II) reoxidized to Fe(III) suggesting that FeCl$_3$ behaves as a catalyst rather than an oxidant (Hirai et al. 2015) (figures 3–6).

### 3.2. XAFS

The early developments of combining auxiliary techniques with x-ray spectroscopy to gain insights in structure formation during the synthesis of catalytic materials and observing the functioning of catalysts in realistic environments have been expanded in recent years. Catalysis research has been the driving force, but many other research fields have benefitted from these developments as well.

Following the pioneering work of the early synchrotrons the third-generation facilities have implemented sample environments from the start including appropriate control software to enable experiments to be performed seamlessly. A very good example of this is the spectroscopy village at diamond (Diaz-Moreno et al. 2018). In summary, four beamlines are in operation which cover hard x-ray microfocus applications (I18, (Mosselmans et al. 2009)), a quick-scanning multipurpose beamline with a wide energy range (2–34 keV to cover most absorption edges) and a large volume where a variety of sample environments can be placed including a solid-state position sensitive detector for XRD, B18 (Dent et al. 2009). The wiggler beamline I20 (Diaz-Moreno et al. 2009) has 2 branches. The first branch, I20-scanning, is a high flux line for dilute fluorescence spectroscopy and includes an emission spectrometer for high energy resolution fluorescence detected (HERFD) as well as non-resonant and resonant x-ray emission spectroscopies. The second branch I20-EDE is an energy dispersive EXAFS beamline (EDE) capable of measuring full spectra down to microseconds.

The early developments of combining auxiliary techniques with x-ray spectroscopy to gain insights in structure evolution during the synthesis of catalytic materials and observing the functioning of catalysts in realistic environments have been expanded in recent years. Catalysis research has benefitted particularly from the application of spectroscopic methods primarily because the elements of interest are present in
too low concentrations (\(\sim\) %) to be amenable to interrogation using scattering techniques. By providing a significant driving force for this purpose, many other research fields have benefitted from these developments. An excellent review of early developments for liquids has already been published (Filipponi 2001).

The capillary cell is a regular fixture on beamlines where catalysis is performed although it is very versatile having been used for the study of liquids and gels including crystallisation and reaction studies (Couves et al 1991, Clausen et al 1993, Newton and van Beek 2010, Beale et al 2011, Rabeah et al 2020) The last two references illustrate the modularity of modern-day synchrotron beamlines allowing multiple techniques (i.e. multiple x-ray measurements or in combination with optical techniques) to be combined together to study sample evolution simultaneously (Beale et al 2011, Rabeah et al 2020). When these types of experiment were first performed over 15 years ago the setup alone would take many days (Nikitenko et al 2008). Miniaturisation and facile integration of the multiple techniques into the x-ray data acquisition process renders these setups tractable nowadays in a matter of hours. A greater amount of space for the sample environment means that it is now possible to integrate large magnetic resonance instruments such as an electron paramagnetic resonance or nuclear magnetic resonance into central facilities (Rabeah et al 2020, Leutzsch et al 2018). One notes

Figure 5. Overview of the highly automated sputter equipment. Reprinted from R Dohrmann et al 2013 with the permission of AIP Publishing.

Figure 6. Schematic representation of the back and front side of the microreactor for operando XAS/MS and DRIFTS/MS studies. A packed-bed catalyst (brown) and glass beads (light grey) upstream of the catalyst bed are depicted on the back side image. Insets show detailed view of the pillars used for retaining the catalyst particles and the thermocouple wells. Reproduced from B Venezia et al 2020. CC BY 3.0.
that the same part of the sample is not interrogated in all cases, but this is less of an issue for soft matter samples.

The stop-flow ‘freeze-cell’ continues to be a go-to setup for elucidating the evolving structure of homogeneous systems and can be used in combination with techniques such as UV–Vis (Venderbosch et al. 2020). These have been largely superseded by the development of flow cells in order to mitigate the influence of the x-ray beam on sample stability (Mesu et al. 2006, Bartlett et al. 2019, Levenstein et al. 2020). To date there appears to be very few actual XAFS studies using such setups largely because of the volume of sample needed for continuous operation.

Continued improvements in source brightness and detector sensitivity over the years has allowed for the collection of more data in shorter timescales. This has been exploited for example for obtaining (a) better time resolution, (b) better spatial resolution and or (c) better sensitivity particularly for photon hungry ‘photon-in/photon-out’ techniques. In the case of (a) perhaps the highest time resolution achieved to date was that of 60 ms resolution when Kong et al. studied the decomposition of (NH4)2[PtCl6], identifying the cis-stereoisomer as an intermediate in the process (Kong et al. 2012). Despite the insight this study gleaned it has to our knowledge, not been repeated. This is largely due to the belief that mechanistic insight into soft and hard matter reaction processes at the nanoscale occurs more slowly than this (s–min.) rendering high time-resolutions redundant. Fundamental bond breaking and making processes in contrast are simply too quick occurring in femtoseconds. Notwithstanding the insight obtained there is an additional challenge when carrying out experiments that require a stimulus (e.g. heat/change in composition) to elicit a sample response in the same time-scale. This is difficult to achieve in catalysis experiments using gas switching as the stimulus as the time resolution is limited by the switching valves to a few ms. However, rapid heating of both liquids and solids can be achieved with lasers and this has been well demonstrated on levitating samples using gas or ultrasound (Egry and Holland-Moritz 2011, Hennet et al. 2011, Nguyen et al. 2017). It should be noted that when high time resolution has not been needed/exploited, it has been possible to measure multiple samples either in series or else simultaneously (Ravel et al. 2010). For these studies it has also been possible to obtain data under well controlled and industrially relevant operation conditions (Martis et al. 2014); the infrastructure required to allow this to happen will bring additional challenges to acquiring data with a higher time resolution. Pressure has also been a useful tool in EXAFS as it has been in SAXS. After early high-pressure experiment using EXAFS on a FeS2 solid sample using a Bridgman-anvil method (Ingalls et al. 1978) the technique has been used widely in the field (Filipponi 2001). Recent developments of a diamond anvil cell with internal heating shows the continuing development of the field for in situ studies (Mijitä et al. 2020).

Imaging (including 2D mapping and 3D tomography) studies are becoming more prevalent nowadays as they allow heterogeneity in the composition or response of a material to be studied and correlated for a more complete understanding of materials performance (Meier and Weckhuysen 2018). Full-field XAFS and mapping studies under in situ or operando conditions are now considered commonplace. In some instances, XAFS has been combined other x-ray imaging modalities i.e. XRF/XRD or combination with optical techniques like IR (Price et al. 2017, Dann et al. 2019). Although the basic capillary design first demonstrated by Clausen et al is still in effect, the modern setup has been engineered to minimise thermal variance in sample heating thereby minimising the effect of temperature on evolving material response. The most recent incarnations have been reported to operate with no dead volume and negligible mass and heat transfer resistances (Venezia et al. 2020).

The spectroscopic techniques derived from the combination of x-ray absorption spectroscopy (XAS) and x-ray emission spectroscopy, such as resonant inelastic x-ray scattering and HERFD XAS have been exploited now for a number of years to yield new insights into the local structure (identity of coordinating ligands) and electronic state, complementary to what can be gleaned from XAFS, particularly since the same types of reaction cell can also be used on these beamlines (Tromp 2015).

Especially in combination with XAFS the technique is particularly powerful in studying calcium oxide formation from hydroxyl gels (Aletru et al. 1999). One area that has always been a strong science driver for the spectroscopy field is catalysis. More recently detailed studies have been possible under well controlled and industrially relevant operation conditions (Martis et al. 2014).

A convergence between x-ray scattering and x-ray spectroscopy has become feasible on modern bending magnet beamlines. By carefully deciding upon the design parameters with respect to flux and energy tuneability it has shown to be feasible to build a combined SAXS/WAXS/XAFS experiment (Nikitenko et al 2008) which also enabled the implementation of several non-x-ray based experimental techniques (Beale et al. 2006). With further improvement in monochromator and detector technology this also has the promise for the future to be able to incorporate time-resolved anomalous scattering experiments. Such a set-up would render a whole gamut of chemical and physical information which certainly in the catalysis field will be very beneficial.

4. Future

With beams getting ever smaller and flux continuing to rise, careful thought must be given to what experiments can truly exploit the new facilities being established/considered. The more so since lab-based instruments are becoming more powerful due to a combination of an increase in the flux that modern technology allows to generate as well as by more efficient detector technology. Lab-based SAXS instruments can now perform time-resolved experiments on the level of 10 seconds/frame using metal jet technology (Adibhatla et al. 2018) and x-ray spectroscopy (Seidler et al. 2014, Zimmermann et al. 2020) systems are becoming so capable that standard material characterisations are becoming feasible. Truly fast experiments, such as those proposed for biomolecules on
XFELs (Levantino et al 2015) will require detector developments beyond what is currently possible even for the XFELs themselves (Sztuk-Dambietz et al 2013, Mozzanica et al 2018).

Another aspect that has to be taken into account is the limit to the x-ray exposure that materials can handle. The increase in brilliance can lead to the destruction of the sample or, as is becoming more recognised, modify the electronic state or phase of the materials. This is unfortunately not limited to the soft matter and biological samples anymore but increasingly recognised in the hard matter and catalysis community as well (Bras and Stanley 2016). Obviously, a prolonged exposure to x-rays, as is required in a time-resolved experiment, is an extra factor in this.

For synchrotron radiation-based experiments to stay relevant in materials science it is clear that the brute force method, by increasing the flux, will not work in future. Hence future developments probably have to be sought in increased experimental sophistication where either the new technical possibilities of the latest multi-bend achromat storage rings, for example, increased coherence or the use of nanosized beams, can be exploited. Alternatively, more elaborate approaches where a combination of sample environments, technique combinations and a new approach to analysing combined data sets might bring the required return in scientific investment.

One new feature of all of the 4th generation facilities proposed or in build is significantly enhanced coherence (Magnuson 2006). While on 3rd generation facilities the coherent fraction of the beam might account for 1%–2% of the total at most, on sources such as Max IV this value can increase to as much as $10^{+9}_\%$ making XPCS possible for SAXS which opens up possibilities for studying chain dynamics in (bio)polymers (Moller et al 2019), microrheology (Papagiannopoulos et al 2005) and even the anomalous dynamics of magnetic anisotropic particles (Pal et al 2018). Coupled to new sub-microsecond detection technologies opens up real opportunities for this technique (Zhang et al 2018).

The intrinsically small beams, <10 μm being delivered at the ESRF after its recent upgrade (Raimondi and Einfeld 2018) and expected on DLS-II, will allow all of the experiment types hitherto exploited to be miniaturised or any heterogeneity to be measured. While currently the preserve of biomaterials such as bone (Liebi et al 2015) and teeth (Schaff et al 2015), it is certain that SAXS tensor tomography will also play a growing role in the future developments in soft condensed matter, for example, the study of foams and orientational heterogeneity in manufactured materials as can be seen now in hard material studies using tomography in other fields (Maire and Withers 2014). Indeed, early examples can already be found in literature looking at microfibrillar-reinforced composite precursors from PEBA and PET (Striebeck et al 2008).

While detectors are rarely developed for SAXS, the early wire chambers (Gabriel et al 1978) and RAPID being one of a limited number (Lewis et al 1997b), the soft matter community are very quick to adapt new detector technologies. Developments in single pixel photon counting technologies including energy discrimination (Martiel et al 2020), integrating detectors will allow new areas to develop. Anomalous SAXS as applied to soft matter has a few devotees (Goerigk et al 2004, Haas et al 2010, Sztucki et al 2012, Ingham et al 2018) but is not currently mainstream. Advances in energy discrimination, especially in ‘windowed’ mode would open up new areas for pink-beam SAXS instruments where spectroscopy could be combined with scattering.

An area where major gains are still to be had in scattering experiments is the field of data analysis. While data reduction (Hammersley 2016, Filik et al 2017) and some preliminary analysis (Wu et al 2020, Doucet et al 2020, Manalastas-Cantos et al 2021), even GiSAXS (Lazzari 2002, Benecke et al 2014, Liu and Yager 2018), is available at some beamlines, with the increases in computing power it should become possible to implement multidimensional correlation spectroscopy to data sets obtained via different experimental techniques (Haas et al 2014) or even reverse Monte Carlo analysis on-line. For mechanical deformations one can envisage a larger role for a combination of SAXS/WAXS with computational methods like digital image correlation Thomas (Engqvist et al 2014). The increased use of artificial intelligence methods might also open up new possibilities (Timoshenko and Frenkel 2019). Just as a thought experiment, one could envisage a polymer extrusion experiment where the data is analysed on-line with AI techniques and the information is fed back to the extruder controls to change the processing parameters. In this way a faster convergence to processing conditions-structure-property relations might be achieved than has hitherto been possible for bulk polymers (30–40 years) and we might deliver expertise levels necessary for processing newly developed polymers which will be required for a sustainable level of materials use.

Many of the things already mentioned above also apply in x-ray spectroscopy. In some cases new undulator insertion devices may replace wiggler on spectroscopy beamlines. The availability of higher energies capable of accessing 2nd row absorption edges, while keeping the beam footprint very small, will allow the ability to analyse smaller samples with lower (i.e. environmentally relevant) concentrations of higher activity materials, including transuranic radionuclides. The same higher energy, and therefore, more penetrating characteristics of the beams will also open up new areas in development of more realistic sample environments. Some examples of areas of science that will open up with new spectroscopy beamlines are metal-based chemotherapy drugs (Anthony et al 2020) which hold much promise for development of selective activity to specific cancer cell types, although the precise cellular targets for many of these compounds remains unclear. Organometallic complexes of ruthenium, iridium and osmium promise this selective activity with low levels of toxicity (Zaki et al 2019, Simpson et al 2019, Renfrew et al 2019). Micro x-ray techniques (x-ray fluorescence imaging and XAS) will offer important insights into the action of these complexes by probing the chemistry and interactions between the introduced agents and their biological targets in a truly spatial manner. This is essential so that investigations of the drug and their interactions are at therapeutically relevant concentrations. This is currently challenging as the signal from the metal compounds is extremely weak. The enhanced flux levels delivered...
using new undulator technologies on 4th generation storage rings will make these measurements possible and expand the usefulness of x-ray spectroscopy.

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Data availability statement

No new data were created or analysed in this study.

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