Planning diffraction experiments at large-scale facilities

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ANSTO

Large-scale facilities

Large-scale facilities are different

1. The radiation has different characteristics
2. You are in an alien environment for a short, intense time
    - Unfamiliar equipment, software, protocols, country
    - Limited or no access before and after
    - Increased attention to safety
3. More expensive (for the taxpayer)
    - Prefer lab source
    - Access is regulated

Types of large-scale facility

- Synchrotron (X-ray)
- Free electron laser (X-ray)
- Reactor (neutrons)
- Spallation source (neutrons)

Synchrotrons

Synchrotrons are brilliant

"Brilliance": amount and divergence of radiation through an area at a given wavelength

Units: photons mm^{-2} $milliradian^{-2}$ s^{-1} per 0.1% bandwidth

Bending magnet: proportional to synchrotron $energy^4$ * current

Lab source: 10^{10}

Bending magnet: 10^{15}

Undulator: 10^{19}

Free electron laser: 10^{33}(peak)

See K Kim, *Nucl. Instr. and Methods* **A**246(1986) 71-76 for discussion of brilliance.

The benefits of brilliance

- Obtain data quickly
- Obtain data from smaller sample

Tunable

Spectrum from most sources is continuous over some range, so can select favourite wavelength using beamline optics

- Choose more/less penetration
- Solve structures using anomalous dispersion differences for heavy atoms
- Adjust wavelength away from an absorption edge
- Beamline optics include monochromators
- Spread out / bring in diffraction spots

Low divergence

Lab source: photon waves are not same phase and radiate outwards.

Synchrotron: beam is naturally transversely collimated

- Peaks spread out less $\Rightarrow$ less overlap $\Rightarrow$ larger unit cells accessible
- Less opportunity for multiple diffraction

Polarisation

Synchrotron beams are almost perfectly polarised in the plane of the ring

- Diffracted intensity falls off horizontally away from the beam
- Equipment is constructed to scan up/down
- Don’t forget to set the appropriate correction in your software

Reasons for going to a synchrotron

- Sample is too small (< ~10 microns)
- Anomalous dispersion required to solve structure
- Unit cell is too large, spots overlap
- Many, many samples, can save time
- You want small crystals/short wavelength to avoid extinction effects
- Want to watch rapid, in-situ changes
- Short wavelength required for larger range of $\sin\theta/\lambda$ (with less drop-off from vibrational motion)

Neutrons

Characteristics of neutrons

Interact with matter differently to X-rays (but interfere like waves)

- Penetrating (many cm)
- Magnetic
- Different atomic cross-section variation compared to X-rays
- No drop-off in form factor with 2θ

Reasons for using neutrons

- Unavoidably big sample (pipeline, rail)
- Need to locate hydrogens accurately
- Need to determine magnetic structure
- Need to distinguish neighbouring elements on the periodic table
- Extreme environments (magnetic, pressure, temperature)
- Measure in-situ with absorbing environment (e.g. batteries)
- Interested in accurate atomic displacement parameters

Issues with neutrons

- Some elements are problematic: B, V, Cd, some rare earths
  - A different isotope will fix the problem ($$)
- Long counting times
- Many elements become radioactive for a while after exposure to the beam
  - Organic compounds do not (C, N, O, H)
  - Sample might have to stay at the facility
  - Manipulating sample may be impossible after first experiment

Neutron sources

- Reactor
  - Continuous wavelength distribution (“thermal”/”cold”)
  - Continuous beam
  - Predictable peak shapes
- Spallation source
  - Pulsed beam
  - Monochromated with choppers
  - Time of flight $\Rightarrow$ velocity $\Rightarrow$ energy $\Rightarrow$ wavelength!
  - No need for 2θ (angular dispersive) measurement
  - Complicated peak shapes

Planning

Diffraction techniques at large-scale facilities

- Single crystal with single rotation axis
  - Laue (significantly reduce data collection time with neutrons)
- Multi axis, triple axis (analyser crystal)
- Small-angle scattering for large-scale structures
- Powder
  - Capillary geometry!
  - Thin films may be possible
  - Detector is vertical

Powder diffraction at synchrotrons

- Always Debye-Scherrer geometry to preserve angular resolution and speed
- Synchrotrons provide excellent angular resolution
  - detect subtle phase transitions
  - solve complex structures where single crystal not available
- Fast measurement means in-situ work possible

BUT

- Very few crystallites in diffracting position $\Rightarrow$ sample requires rotation for good randomisation

Powder diffraction at reactor sources

- “High” resolution: comparable to, or worse than, lab X-ray resolution
- Easiest way to determine magnetic structures
- Often “finishing off” previous X-ray work by determining light atom positions
- Frequent use of non-ambient environment:
  - 50mK to 1600C
  - 12 Tesla
  - high pressure

Diffraction at spallation sources

- Really bulky sample environment
  - 2 GPa / 2000K (PLANET, JPARC)
- Better peak resolution (powder)
- Fast single-crystal collection
  - surround the sample with detectors

Single-crystal diffraction at synchrotrons

- Small crystals, fast collection
- Often optimised for either chemical crystallography or macromolecular crystallography
- Macromolecular is the easy one (from an instrumentation point of view)!
  - Many,many spots of same order of magnitude intensity
  - Large $\sin\theta/\lambda$ not required
  - Limited number of possible space groups
  - No need for multiple crystal positioning axes
  - Just send a robot cartridge!

Single crystal diffraction at neutron sources

- Area detector + reactor source takes ~ weeks
- Laue + reactor source takes ~ day
- Spallation source fastest

Accessing large-scale facilities

Usually you will write an application through a user proposal portal. Check the facility website.

Applications are generally judged on:

- Scientific worth
- Technical feasibility

You are more likely to be successful if:

- You clearly explain the science
- You explain the beamtime calculation
- You justify the choice of instrument for your problem
- You explain how you will process and analyse the data
- You have a good track record

Planning: know your instrument

Talk to the instrument scientist. Questions to think about:

- Single crystal size: what are the beam dimensions on the sample? How much does the sample move if/when rotated ("sphere of confusion")
- Detector: what is the dynamic range of the detector? Will you need to re-measure due to saturated pixels? What corrections are required? What corrections are performed?
- Geometry: what is the maximum 2θ that is measurable? Is this in/out of the plane of polarisation?
- How is the sample mounted? Will the mount sag if the crystal is moved? If powders, how big is the capillary?
- Look at previous publications from the instrument
- Look at the instrument publication

Planning: know your sample

(As well as possible in the circumstances)

- Could there be water of crystallisation in the sample (problem for neutrons)?
- Will your sample survive long enough in the beam? Do you have spares?
- Have you characterised the sample as much as possible in the lab?

Planning: know your data

- Can you report and reproduce your on-site data reduction steps?
- Will the raw data be available permanently from the facility? Does your institution have a repository?
- Will you be able to re-extract the data once you are off-site?
- Are the data formats well-documented?

Planning your experiment: Time is valuable

- Make a schedule
  - Account for heating and cooling time
  - Use a spreadsheet to update as things go wrong...
- Be prepared to examine data on-site
  - Do you know the local software?
  - Should you bring your own software?
- Take spare samples
- Be aware of safety
- Have enough people and skill:
  - 2 working + 1 resting per 8 hrs
  - 1 of those 2 is experienced

Designing the experiment

Experimental decisions I

Single crystal data collection strategy:

- Step size in ω ("slicing")
  - Smaller $\Rightarrow$ Larger data volume
  - Smaller $\Rightarrow$ Better weak peak fitting
  - Smaller $\Rightarrow$ Longer data collection
  - Smaller $\Rightarrow$ Less peak overlap
- Choice of wavelength(s)
  - Collect at two wavelengths for structure solution
  - Avoid absorption edges (high background adjacent, on short wavelength side)

Experimental decisions II

- Range of data collection
  - A full rotation allows better absorption correction and averaging
  - More than one χ position allows access to all reciprocal space
    - May be a crucial axis for space-group determination
  - $\sin 2\theta / \lambda < 1.0$ (chemical crystallography) / whatever your crystal provides (protein)
- Do you need multiple collections?
  - crystal decay in the beam
  - saturated pixels