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Structure and Properties of Functional Materials

Exercise Set 1

Friday, 11 January, 2013

1. *For discussion:*

   (a) Suppose two diffraction patterns of the same crystal are measured: one recording all spots with $Q \leq 7\,\text{Å}^{-1}$, the other recording all spots with $Q \leq 10\,\text{Å}^{-1}$. Explain why the uncertainty in the calculated atomic positions will be greater for the first than for the second experiment.

   (b) How would you expect the diffraction patterns of a block-shaped crystal (like a grain of salt) and a long, needle-shaped crystal of the same material to differ?

Solution: Both parts are intended to be solved using the convolution theorem. In (a), cutting out the spots above, say, $7\,\text{Å}^{-1}$ is equivalent to multiplying the diffraction pattern by a "top-hat" function

$$T(Q) = \begin{cases} 1 & Q \leq 7\,\text{Å}^{-1} \\ 0 & Q > 7\,\text{Å}^{-1} \end{cases}$$

Thus in real space we *convolute* the crystal structure by the inverse Fourier transform of this function. In fact this will be something complicated involving Bessel functions, but all we need to know here is that the wider our cutoff function, the narrower its inverse Fourier transform will be. So the crystal structure calculated from the first diffraction pattern will be blurrier than from the second.

In (b), we have the opposite situation: we are multiplying our crystal in real space by a cutoff function, giving a convolution of the diffraction pattern in reciprocal space. The Fourier transform of the needle-shaped cutoff will be very narrow in the direction parallel to the needle, and broad in the directions perpendicular to it. So the diffraction spots will be sharp in the direction parallel to the needle and fuzzier in the perpendicular directions, whereas for the cubic crystal they will be more isotropic.

2. Uranium tetrafluoride, which in its molten state can be used to fuel molten-salt nuclear reactors, has room-temperature lattice vectors (in Å)

$$\mathbf{a} = 12.81\mathbf{i}$$
$$\mathbf{b} = 8.40\mathbf{j}$$
$$\mathbf{c} = -6.34\mathbf{i} + 8.67\mathbf{k}$$

where $\mathbf{i}, \mathbf{j}, \mathbf{k}$ are the orthogonal unit vectors. Calculate the reciprocal lattice vectors for this crystal. Sketch them and the real lattice vectors on the same diagram. Calculate the real and reciprocal cell volumes.

Solution: This is a straightforward application of the formula

$$\mathbf{a}^* = 2\pi \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}}$$

and the equivalents for **b** and **c**. The denominator – which is just the crystal volume – is

$$V_{\text{cell}} = \mathbf{a} \cdot \mathbf{b} \times \mathbf{c} = (12.81\mathbf{i}) \cdot (72.828\mathbf{i} + (\text{whatever})\mathbf{k}) = 932.9\,\text{Å}^3$$

which gives a reciprocal cell volume of

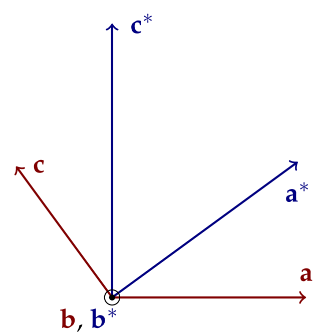
$$V^*_{\text{cell}} = \frac{(2\pi)^3}{V_{\text{cell}}} = \frac{(2\pi)^3}{932.927\,\text{Å}^3} = 0.2659\,\text{Å}^{-3}$$

and unit cell vectors, in Å^{-1},

$$\mathbf{a}^* = 2\pi \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}} = 2\pi \frac{72.828\mathbf{i} + 53.256\mathbf{k}}{932.9} = 0.4905\mathbf{i} + 0.3587\mathbf{k}$$
$$\mathbf{b}^* = 2\pi \frac{\mathbf{c} \times \mathbf{a}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}} = 2\pi \frac{111.063\mathbf{j}}{932.9} = 0.7480\mathbf{j}$$
$$\mathbf{c}^* = 2\pi \frac{\mathbf{a} \times \mathbf{b}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}} = 2\pi \frac{107.604\mathbf{k}}{932.9} = 0.7247\mathbf{k}$$

(from which the volume can be confirmed as a check).

The diagram is easiest to draw in the xz plane:



Note that $\mathbf{a}^*$ is perpendicular to **b** and **c** (and so on), and that longer vectors in real space correspond to short ones in reciprocal space, as we expect. Note also that there is no unique scale with which to draw real and reciprocal lattice vectors on the same diagram, since they have different units and are thus not directly comparable. (This is similar to diagrams in mechanics showing, for instance, velocity and force vectors together.)

3. What is the maximum value of Q measurable with copper $K\alpha$ radiation of wavelength $\lambda = 1.5418\,\text{Å}$? Estimate how many distinct diffraction spots would theoretically be measurable if a crystal of uranium tetrafluoride (see the previous question) were put in a beam of this radiation.

Solution: The maximum value of Q attainable is $4\pi/\lambda = 8.1505\,\text{Å}^{-1}$. We can estimate the number of diffraction spots by

$$\frac{\text{volume of allowable region in } Q\text{-space}}{\text{volume per reciprocal lattice point}} = \frac{\frac{4}{3}\pi Q_{\text{max}}^3}{V_{\text{cell}}^*} = \frac{\frac{4}{3}\pi(8.1505)^3}{0.2659} \approx 8530$$

This isn't exactly a formula we have seen in class so it's worth while checking you understand exactly where it comes from.

4. Let

$$f(x) = \begin{cases} e^{-x} & x \geq 0 \\ 0 & \text{otherwise;} \end{cases} \qquad g(x) = \begin{cases} xe^{-x} & x \geq 0 \\ 0 & \text{otherwise.} \end{cases}$$

(a) Find the Fourier transform of $f(x)$.

Solution:

$$\mathcal{F}\big(f(x)\big) = F(Q) = \int_0^\infty e^{-x}e^{iQx}\ \mathrm{d}x = \left.\frac{\exp\big((iQ-1)x\big)}{iQ-1}\right|_{x=0}^{\infty} = 0 - \frac{1}{iQ-1} = \frac{1}{1-iQ}$$

(b) Show that $(f \otimes f)(x) = g(x)$.

Solution:

$$\begin{aligned}(f \otimes f)(x) &= \int_{-\infty}^{\infty} f(t)f(x-t)\ \mathrm{d}t = \int_0^x e^{-t}e^{t-x}\ \mathrm{d}t \quad \text{(if } x>0\text{; zero otherwise)} \\ &= e^{-x}\int_0^x \mathrm{d}t = xe^{-x} \quad \text{(if } x>0\text{; zero otherwise)} \quad = g(x) \quad \text{as required.}\end{aligned}$$

(c) Hence use the convolution theorem to evaluate the Fourier transform of $g(x)$. Check your answer by direct calculation.

Solution: By the convolution theorem

$$\mathcal{F}(f \otimes f) = \mathcal{F}(f) \times \mathcal{F}(f) = [F(Q)]^2 = \frac{1}{(1-iQ)^2}\,.$$

On the other hand, calculating directly gives

$$\begin{aligned}\mathcal{F}\big(g(x)\big) &= \int_0^\infty xe^{-x}e^{iQx}\ \mathrm{d}x = \left. x\frac{1}{iQ-1}e^{x(iQ-1)}\right|_{x=0}^{\infty} - \int_0^\infty \frac{1}{iQ-1}e^{x(iQ-1)}\ \mathrm{d}x \quad \text{(by parts)} \\ &= 0 - \left.\frac{1}{(iQ-1)^2}\ e^{x(iQ-1)}\right|_{x=0}^{\infty} = 0 - \left(-\frac{1}{(iQ-1)^2}\right) = \frac{1}{(1-iQ)^2} \quad \text{as before.}\end{aligned}$$