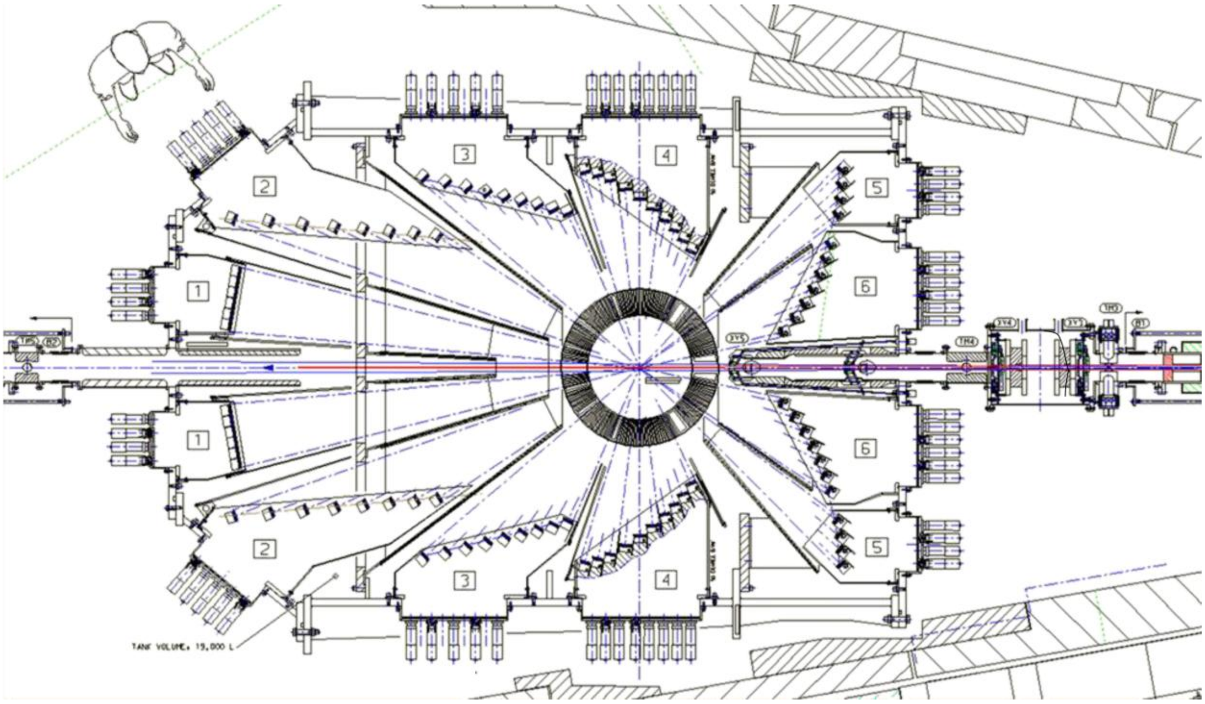
Supplementary Information S1: Some details of the upgraded Polaris diffractometer

Basic construction

The basic construction of the Polaris diffractometer, and its detector banks is shown in the diagram below, which gives a horizontal cross-section of the instrument. The incident neutron beam runs from right to left and so the numbered banks are at progressively higher Bragg angles (note: the detectors labelled 5 and 6 in the diagram are treated as a single detector bank (bank 5) during data reduction).

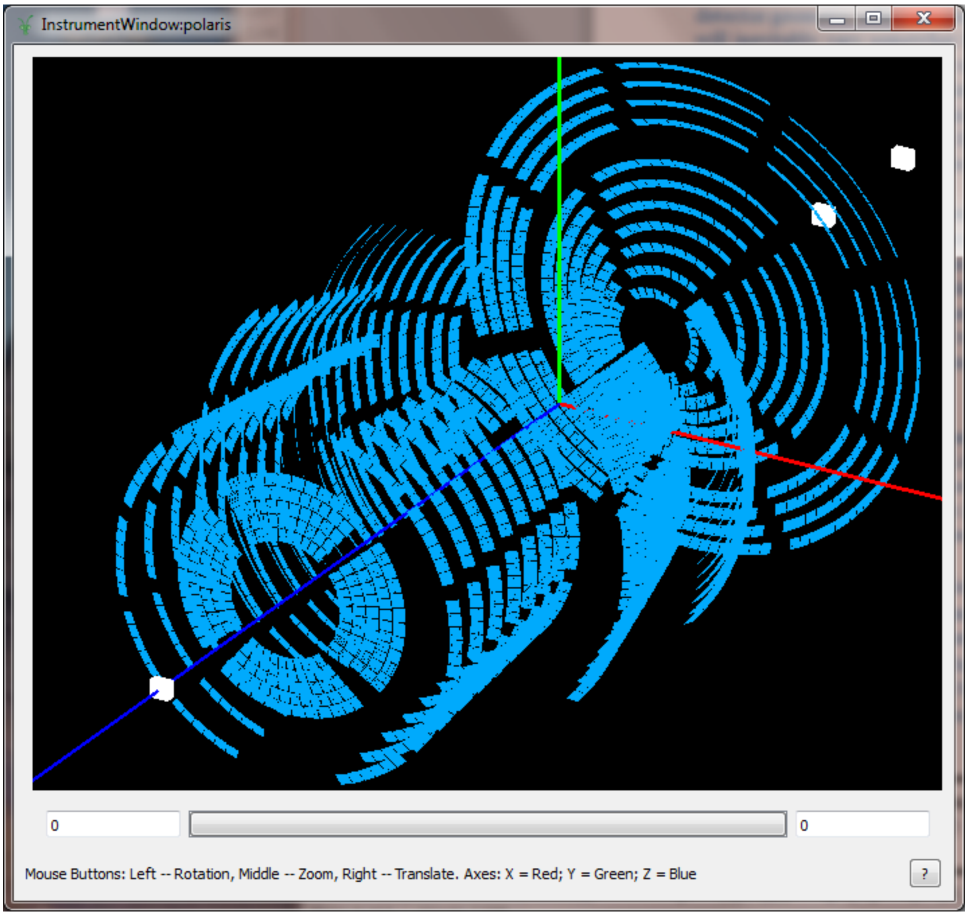


Calibration

All instrument calibration and data normalisation was done using the Mantid software package (an open source framework that supports high-performance computing and visualisation of scientific data, created to manipulate and analyse neutron and muon scattering data).

(Reference: Mantid (2013): Manipulation and Analysis Toolkit for Instrument Data. Mantid Project. http://dx.doi.org/10.5286/SOFTWARE/MANTID).

Calibration of the detector banks on the upgraded instrument was a 2-stage progess. Based on a geometric description of the detector arrangement (using "ideal" flight paths and scattering angles derived from engineering drawings), see figure below, the Mantid *AlignDetectors* algorithm does an initial focusing of the data into *d*-spacing from the time-of-flight units of the data collected. Because the actual geometry achieved during construction and assembly of the detectors and diffractometer will inevitably vary somewhat from this ideal layout, small offsets still need to be applied to the converted *d*-spacings in order to achieve the final focusing of the data. The offsets were determined using the Mantid *CrossCorrelate* algorithm: an arbitrary reference detector element was chosen and a cross correlation function calculated between it and the data in each of remaining elements, with the maximum in this function for each detector giving the shift in x-axis position (positive or negative) required to put all the detectors in each bank on the same *d*-spacing scale.



Mouse Buttons: Left -- Rotation, Middle -- Zoom, Right -- Translate. Axes: X = Red; Y = Green; Z = Blue

Figure - isometric view of the geometry of the Polaris detector banks as described by the Mantid *Instrument Parameter File*. The sample position is at the intersection of the three axes.

Peak Shapes

The observed peak shape in time-of-flight powder diffraction is complex and asymmetric, combining rising and falling exponential functions (arising, respectively, from the "fast" neutron production in the ISIS target and the subsequent slowing down of these neutrons in the moderator) with a symmetric broadening function due to the finite dimensions of the moderator, sample and detectors. In the commonly used Rietveld refinement software packages GSAS and Fullprof this shape is well-modelled by a convolution of two back-to-back exponential functions with a pseudo-Voigt function (which itself is a linear combination of Gaussian and Lorentzian functions).

(References:
A.C. Larson and R.B. Von Dreele, "General Structure Analysis System (GSAS)", Los Alamos National Laboratory Report LAUR 86-748 (2000).
J. Rodriguez-Carvajal, Physica B. (1993), 192, 55.
J. Rodríguez-Carvajal, Recent Developments of the Program FULLPROF, in Commission on Powder Diffraction (IUCr) Newsletter (2001), 26, 12-19.)

Resolution

The $\Delta d/d$ resolution of a time-of-flight powder diffraction pattern, manifest in the width of the peaks, varies dramatically with detector angle, 2θ, and for this reason the detector elements are grouped into a number of discrete banks, with each bank containing elements covering a similar *d*-spacing range and having a similar resolution. Detector banks at high 2θ angles have the sharpest Bragg reflections but only measure to relatively low maximum *d*-spacings, whereas detectors at low 2θ angles have poor resolution (wide peaks) but are able to access much longer *d*-spacings (see Table below).

The high flux of very short wavelength neutrons produced in the spallation process and lack of a form factor in the scattering process combined with the $\Delta d/d = constant$ resolution function enables diffraction data to be collected down to very short *d*-spacings while minimising the effects of reflection overlap. This is in complete contrast to the situation which may be achieved on a constant wavelength diffractometer (X-ray or neutron), and the wide $\sin\theta/\lambda$ range thus available allows excellent refinement of thermal vibration parameters.

Detector Bank		2θ Range (/°)	Secondary Flight path (/m)	Solid Angle (/ster)	$\Delta d/d$ resolution (%)	d_{max} (/Å)
very low angle	1	6 - 14	2.25	0.26 (0.01)	2.7	> 40
low angles	2 3	19 - 34 40 - 66	2.36 - 1.30 1.56 - 0.92	1.04 0.92	1.5 0.85	13.5 7.0
90 degrees	4	75 - 113	1.08 - 0.71	1.33	0.51	4.1
back-scattering	5	135 - 167	1.54 - 0.8	2.12	0.30	2.65

Normalisation of Data

Normalisation of time-of-flight diffraction data entails accounting for the fact that both the intensity of the incident polychromatic ("white") neutron beam and the efficiency of the ZnS scintillator in the detectors vary as a function of wavelength, which itself is proportional to both time-of-flight and measured *d*-spacing. These combined effects can be quantified by measuring an isotropically scattering sample, such as vanadium: for this purpose a 5mm diameter vanadium rod is used on Polaris.

The data from the vanadium rod first have an empty diffractometer (i.e. no sample) data set subtracted to account for the sample independent instrument background, before being corrected for wavelength-dependent absorption effects (with the Mantid *CylinderAbsorption* algorithm) and finally are smoothed to remove the (very weak) Bragg reflections present (using the Mantid *SplineBackground* algorithm).