Structure of hydrogenous liquids: separation of coherent and incoherent cross sections using polarised neutrons

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Abstract. The determination of the coherent structure factor of hydrogenous liquids is very difficult: while X-rays are barely sensitive to hydrogen, neutrons results still lack accuracy due to the contamination of the scattering intensities by a huge spin-incoherent signal from the $^1$H atoms. Using polarised neutrons with polarisation analysis, one can experimentally separate the coherent and incoherent contributions to the scattered intensity. We present the upgrade of the D3 polarised hot neutron diffractometer at ILL to study hydrogenated liquids. We show first data obtained from a test sample of water and detail the data reduction leading to an unprecedented accuracy in the extraction of the coherent signal, representative of the structure.

1. Introduction

The determination of the coherent structure factor of hydrogenous liquids by the usual scattering methods is very difficult: the scattering of X-rays by 1-electron hydrogen is usually too weak to be detected, while neutron scattering is largely dominated by incoherent scattering (incoherent cross-section $\sigma_i = 80.27(6)$ barns, to compare to the coherent cross-section $\sigma_c = 1.7523(10)$ barns \cite{1}). As a result, the parasitic incoherent background may reach over 90\% of the measured signal, as seen \textit{e.g.} in the case of light water $\text{H}_2\text{O}$ \cite{2}\cite{3}. Theoretical efforts to estimate the incoherent neutron background have not yet led to a unique solution and, as a result, the precise nature of the hydrogen bond is still highly debated.

In the case of isotopic $^1$H hydrogen, the incoherent scattering is solely due to the disorder of the nuclear spins ("spin-incoherent"). It can be shown that in that case, the scattering of the neutrons partially (2/3) reverses their polarisation ("spin-flip", SF), while coherent and isotope incoherent scattering do not ("non-spin-flip", NSF) \cite{4}. As a result, the coherent and incoherent intensities are linear combinations of the spin-flip and non-spin-flip measured intensities, Eqs. (1) and (2).

\begin{equation}
I_{\text{coh}}(Q) + I_{\text{isotope inc}}(Q) = I_{\text{NSF}}(Q) - \frac{1}{2}I_{\text{SF}}(Q)
\end{equation}

\begin{equation}
I_{\text{spin inc}}(Q) = \frac{3}{2}I_{\text{SF}}(Q)
\end{equation}
Using polarised neutrons with polarisation analysis, one can then work around the high-background problem and experimentally separate the coherent and incoherent contributions to the scattered intensity. Note that Eqs. (1) and (2) only take the elastic scattering (coherent and incoherent) into account. Corrections for inelasticity, multiple scattering... are beyond the scope of this paper.

2. Instrument

Although the above described principle is quite simple, very few structural studies of hydrogenated liquids using this technique have as yet been reported [5][6]. The main reason lies in a former shortcomings of the experimental technique: studies of liquids need measurements up to high momentum transfers $Q$ (typically 20-25 Å) for the purpose of Fourier transforming [7], hence need the use of neutrons with a relatively short wavelength, typically 0.4-0.5 Å. At these wavelengths, the use of supermirrors for polarisation analysis is excluded (very small critical angle), and the use of polarising crystal analysers is limited (small take off angles, implying the need of either forbiddingly large crystals, or very long distances. The situation has changed with the advent of spin filters based on polarised $^3$He [8] and the ensuing developments allowing their easy use even at short neutron wavelengths [9].

The D3 diffractometer of the Institut Laue-Langevin (ILL) in Grenoble, initially built for magnetic (elastic) studies on single crystals using polarised neutrons has been upgraded for the study of liquids (Fig. 1). The neutron beam on D3 comes from the hot source and the covered wavelength range is 0.4 Å to 0.84 Å. The polarising monochromator is a Heusler, Cu$_2$MnAl, single crystal. Guide fields along the beam path ensure the preservation of the neutron polarisation. A monitor before the sample serves for normalisation of the measured intensities. The neutron polarisation can be flipped either before or after the sample using a nutator. The $^3$He spin filter is situated just before the single $^3$He detector, on the detector arm. The detector is scanned over a total angular range of 4° to 120°, with typical data acquisition times of 1-2 minutes/angular step, both polarisation channels being measured at each step. Using a wavelength of 0.52 Å, the covered $Q$-range is 0.8 to 21 Å$^{-1}$. With a beam size of 12 x 22 mm$^2$ and an annular vanadium sample cell, with a 1 mm thick annular space (to minimise multiple scattering), the amount of sample in the beam is about 0.9 cm$^3$.

![Figure 1. The D3 diffractometer at ILL, modified for the study of liquids: principle (left) and top view (right).](image)

Since the $^3$He polarisation in the spin filter decays over time, typically loosing about 5-10% per day, the analysing power has to be monitored. For this purpose, a silicon single crystal is
glued to the top of the sample cell and regularly driven into the beam via a motorised translation. The polarisation of the beam is measured by comparing the SF and NSF intensities of a Si Bragg peak.

In the instrument upgrade, particular care has been taken in the shielding to minimise the instrument background. Typical levels away from the vicinity of the direct beam are of the order of 1 count/s.

3. Data reduction

The first step of the data reduction is the accurate determination of the spin-filter efficiency, and its relaxation rate. Following [8], the transmissions of the up \( T^+ \) and down \( T^- \) neutron polarisations are:

\[
T^\pm = \frac{1}{2} e^{-O(\lambda)(1 \mp \text{Pol}_{^3\text{He}})},
\]

where \( O(\lambda) \) is the opacity, proportional to the \(^3\text{He} \) pressure \( P \), the length of the spin filter \( l \) and the wavelength \( \lambda \). At 295 K, \( O(\lambda) = 7.28210^{-2} P[\text{bar}] l[\text{cm}] \lambda[\text{Å}] \). \( \text{Pol}_{^3\text{He}} \) is the \(^3\text{He} \) polarisation, \( \text{Pol}_{^3\text{He}} = \text{Pol}_{^3\text{He}}^0 e^{-t/T_1} \), where \( t \) is the time of the measurement, \( \text{Pol}_{^3\text{He}}^0 \) the \(^3\text{He} \) polarisation at \( t = 0 \), and \( T_1 \) is the relaxation time. The polarisation measurements on a Bragg peak actually give access to the product of the initial beam polarisation and the spin-filter analysing power (efficiency). Fig. 2 shows a typical result. Currently on D3, \( T_1 \) is of the order of 100 to 120 hours, and the polarisation of the small beam impinging on the single crystal used for calibration is usually of the order of 90%. We must note at this point that, since the single crystal used for calibration of the polarisation is much smaller than the sample cell, we also measure the full beam polarisation using a larger Si wafer to correct for a possible different overall polarisation of the full beam.

\[\text{Figure 2. Calibration of the spin filter analysing power: fit of the relaxation time } T_1 \text{ and the incoming beam polarisation}\]

Figure 3 shows the different steps of the data reduction for a light water H\(_2\)O sample, from the top left panel (measurement) to the bottom right panel (coherent and incoherent cross sections). The first step (top right) is the correction for the decay of the spin filter analysing power. Once this critical step has been performed, one can average the corrected scans, hence improving the statistics (bottom left), and extract the coherent and incoherent cross sections (bottom right). In the figure, the coherent part, representative of the correlations, had to be blown up by one order of magnitude for visibility (see the different scales). A measurement with unpolarised beam, as in [2][3] is actually the sum of both spectra and, as pointed out in the introduction, widely dominated by the incoherent signal.
4. Discussion

Obviously, the uncorrected incoherent and coherent data in Fig. 3, while showing the power of the method, should not be used to extract correlation functions without a more careful treatment of the NSF and SF corrected and averaged intensities. For example, one must take into account the fact that the thin container is made of Vanadium, which is a mostly spin-incoherent scatterer, giving signal in both polarisation channels following the ”1/3 - 2/3” rule from Eqs. (1) and (2). As usual in that type of measurement, a more tricky correction comes from multiple scattering, for which the usual treatments have to be adapted to take the neutron spin state into account (scattering twice in the SF channel will actually give intensity in the NSF channel...). Details on the current state of the analysis can be found in [10]. Another approach is to use the polarised neutron results to model the incoherent contribution to the scattering [11], and use this knowledge in the analysis of unpolarised data.

5. Conclusion

The D3 diffractometer of the ILL is now fully operational for the study of liquids using polarised neutrons, and scripts have been developed for on-line data reduction. The data acquisition is currently slower than on fully dedicated instruments like D4 at ILL [12] due to the absence of a wide-angle spin filter and a multi-detector. Typical measuring times are 1-2 days per sample, which is fortunately not forbiddingly long. Using D3 for accuracy in the case of the non-
deuterated samples, and complementing with unpolarised results for more deuterated samples may be an efficient option. A future upgrade will be the installation of a vacuum chamber to further minimise the instrument background, especially in the vicinity of the direct beam and allow measurements down to lower $Q$ values. As an ultimate upgrade, a wide-angle spin-filter for short wavelengths should be developed, in association with the use of a multidetector.

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