

Determination of the density of states of liquid light and heavy water as a function of temperature

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Abstract. Although light and heavy water in liquid state are the most widely used moderator and reflector materials in nuclear reactors, there is a lack of knowledge of the vibrational density of states of as a function of temperature that match the quality of data achievable with the present-day neutron facilities. As a consequence, the thermal scattering libraries currently available are based on very old experimental data. In the last three decades newer measurements of the water density of states were made, but they are not suitable for the calculation of scattering kernels, because the accuracy over the full energy-range was not good enough, or the temperature region covered was too short. In this work we show new results of the density of states of light and heavy water measured at 300, 330 and 360 K, at spectrometer MARI (ISIS, UK). Non-trivial multiple-scattering and multiphonon correction, specially devised for this purpose were applied. The corrections also involved the previous knowledge of total cross sections and thermodynamic parameters.

1. Introduction

Since liquid light and heavy water are the most widely used moderator and reflector materials in nuclear reactors, the knowledge of their neutron cross sections is a permanent requirement of the nuclear Engineers. Also, the dynamic features involved in the vibrational density of states constitutes a key piece of information, that is included in the usual nuclear libraries (e.g. ENDF) employed in the calculation of cross sections (code NJOY), and Monte Carlo simulations (MCNP). Despite this fact, the thermal scattering libraries currently available for these materials [1] are based on experimental data obtained and processed during the '60s. The density of states obtained from the measurements by Haywood and Page [2] is still the basis for the scattering kernels available in the latest releases of ENDF/B and JEFF. These thermal scattering libraries are far from perfect: when the computed total cross section is compared to experimental values, differences of up to 50 % arise. In view of this we undertook a work project to explore the density of states of liquid water at different temperatures, with the most updated neutron facility resources. In this work we show the densities of states obtained in light and heavy liquid water at different temperatures at spectrometer MARI (ISIS, UK).

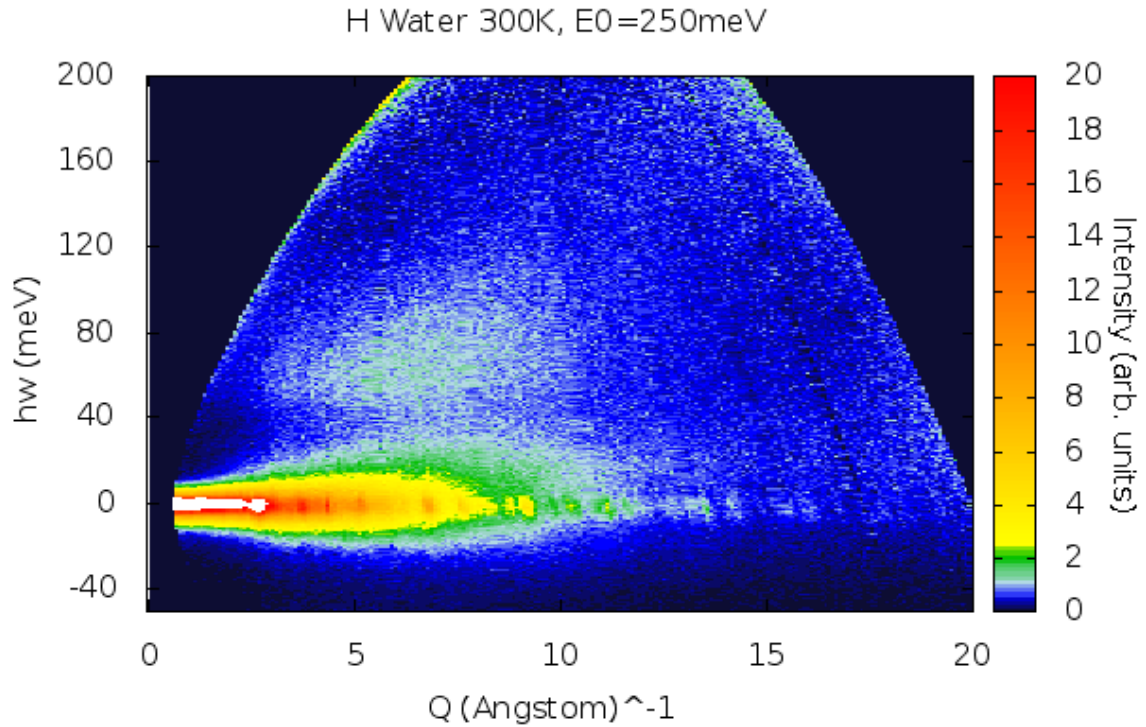


Figure 1. Map of the intensity of the scattered neutrons in H₂O at 300 K, as a function of the transferred energy ($\hbar\omega$) and momentum (Q), at spectrometer MARI (ISIS, UK).

2. Experimental

The experiment was performed at MARI, a direct geometry chopper spectrometer located at the ISIS pulsed neutron facility, Rutherford Appleton Laboratory (Oxfordshire, U.K.). The incident energy was 250 meV, with an energy resolution of about 1 meV. The samples were light water and (99.99 %)-deuterated water, contained in a hollow cylindrical aluminum can placed perpendicularly to the incident beam, of dimensions 4.5 cm and 4.2 cm as outer and inner diameter respectively, and 4.9 cm height, with Aluminum walls thickness of 0.5 mm. The measurements were carried out at 300, 330 and 360 K. In Fig. 1 we show a typical map of the scattered intensity in the Q - ω plane.

3. Multiple scattering corrections

3.1. Fundamentals

The experimentally measured magnitude is the *double differential macroscopic cross section*, i.e. the probability that an incident neutron with a wavevector \mathbf{k}_0 will emerge from the sample-container set with a wavevector \mathbf{k} . Its expression is

$$\frac{d^2\Sigma}{d\Omega dE} = \frac{N\sigma_b}{4\pi A} \frac{k}{k_0} s(Q, \varepsilon). \quad (1)$$

In this Eq. (1) $s(Q, \varepsilon)$ is the same as $s(\mathbf{k}_0, \mathbf{k})$, the effective scattering function proposed by Sears [3], that can be decomposed in a part due to neutrons scattered once in the sample $s_1(Q, \varepsilon)$, another due to scattering once in the can $s_C(Q, \varepsilon)$, and a third due to multiply scattered neutrons (with any combination of sample-can scattering events) $s_M(Q, \varepsilon)$:

$$s(Q, \varepsilon) = s_1(Q, \varepsilon) + s_M(Q, \varepsilon) + s_C(Q, \varepsilon). \quad (2)$$

3.2. Correction procedure

The computer multiple-scattering correction procedure we devised is based on Ref. [4]. The Monte Carlo code samples the density of neutrons in the steady state regime. To this end Copley's scheme [5] provides an efficient method, that consists in generating neutron histories

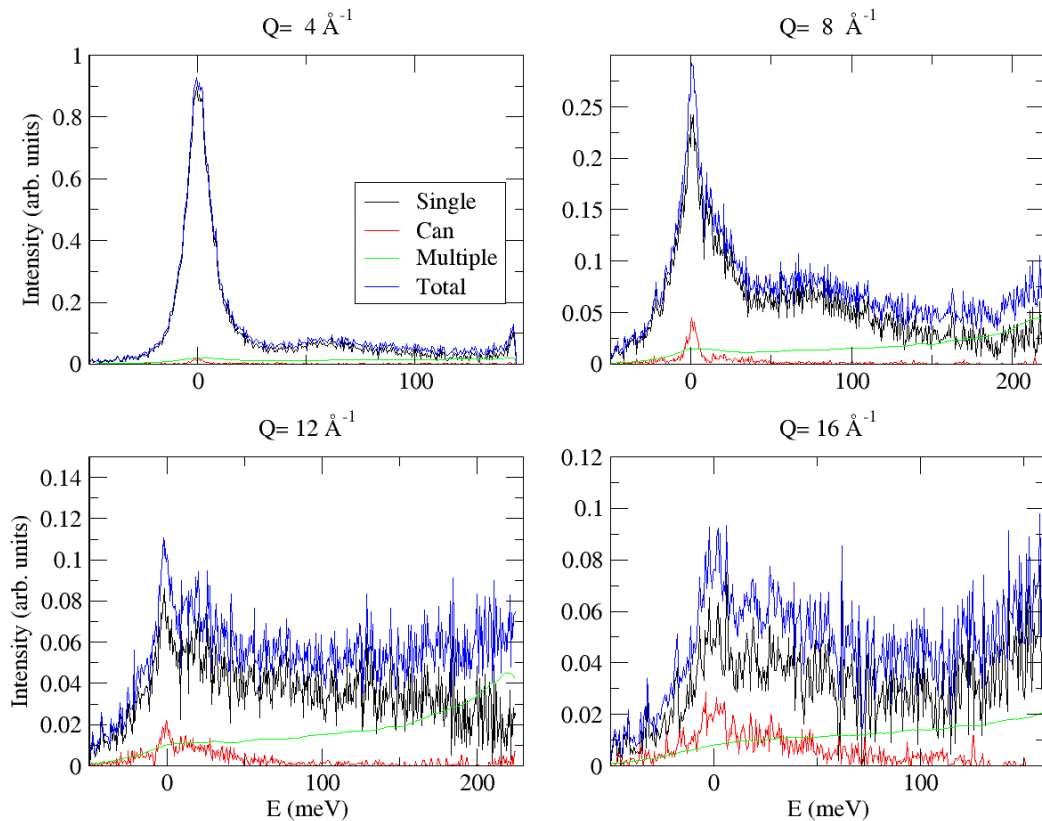


Figure 2. Detail of the calculated components of the observed spectra, for the light water sample at 300 K, and several values of Q , after the convergence of the iterative correction process.

biased in such way that the neutron never leaves the sample nor is absorbed. To compensate this bias, a weight (that is initially 1) is computed for the history, that decreases at every path traversed and at every scattering step. Neutron histories are originated in a random point of the sample surface that faces the incoming beam. The distance traveled by the neutron between two scattering steps is determined by the mean free paths of the materials that the neutron has to traverse at the current flight direction and energy E , to emerge from the sample. After the scattering event, new energies and directions of flight are randomly sampled.

The procedure is iterative. In the first step the scattering law is taken from the experimental data. The program calculates the different contributions to the observed spectra according to

Eqs. (1) and (2). The experimental data are corrected with factors by multiple scattering and beam attenuation effects [4], and introduced in the Monte Carlo code for a new run. The process converges typically after 5 runs. Fig. 2 shows the components of single and multiple scattering, as well as the cell contribution to the observed scattering. The total calculated scattering coincides with the original raw data, thus showing the good convergence of the method.

4. Multi-phonon corrections

The route to evaluate the generalized density of states is based on Price and Carpenter [6] method, that starts from the incoherent approximation. This method serves to average out substantial Q dependence present in the structure factor of the samples.

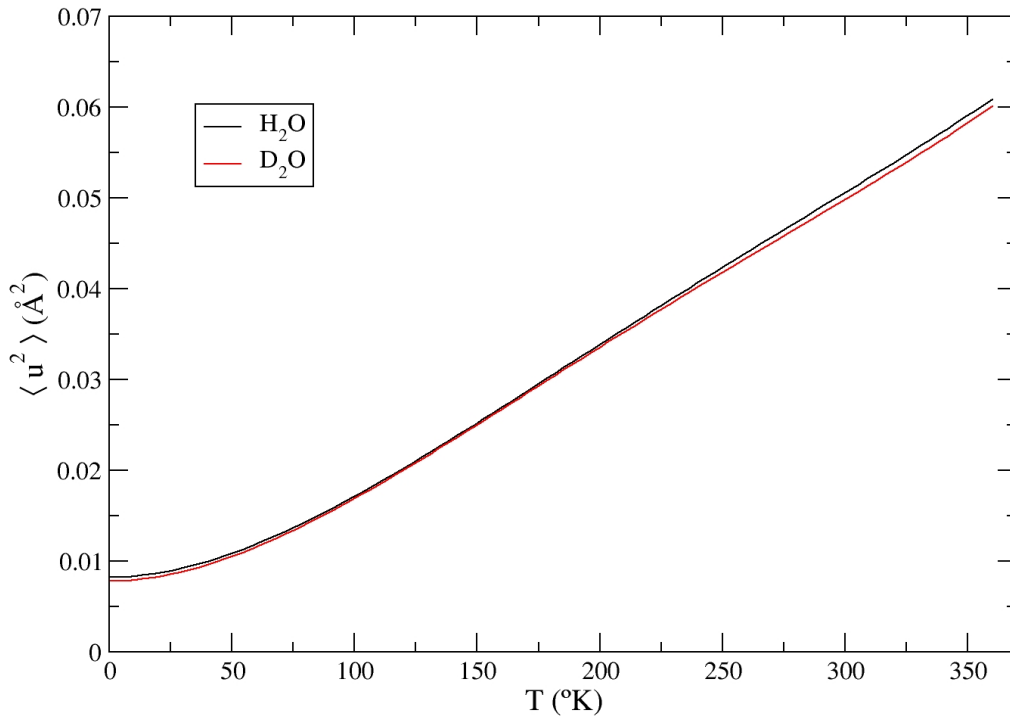


Figure 3. Mean-square displacements of H_2O and D_2O based on Leadbetter's [7] thermodynamic calculations.

The starting point of our method is the standard phonon expansion

$$S(Q, \omega) = e^{-2W} \sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{\hbar^2 Q^2}{2M} \right) u_n(Q, \omega), \quad (3)$$

where the one-phonon term is

$$u_1(Q, \omega) = \frac{Z(Q, \omega)}{\omega} [n(\omega) + 1], \quad (4)$$

M is the molecular mass, $n(\omega)$ is the boson occupation number, and $Z(Q, \omega)$ the density of states. The Q -dependency of u_n and Z reflects the coherent behavior of the system, in the framework of this incoherent approximation. The Debye Waller factor $2W$ is

$$2W = \frac{1}{3} \langle u^2 \rangle Q^2 \quad (5)$$

and the n -th phonon term can be calculated with

$$u_n(Q, \omega) = \int_{-\infty}^{\infty} d\omega' u_{n-1}(Q, \omega - \omega') u_1(Q, \omega') \quad (6)$$

Eqs. (3) to (6) constitute the phonon expansion for each Q in the incoherent approximation. The procedure employed in this work consists in treating the uncorrected data as if it were single-phonon, and to calculate the multi-phonon contribution with the phonon expansion. The data are then corrected by a factor [4], and the phonon expansion is re-calculated. The iterative process converges typically after 7 runs.

The calculation of the multi-phonon components involve the knowledge of the molecular mean square displacement. In this work we employed the data calculated by Leadbetter [7]. In Fig. 3 we show $\langle u^2 \rangle$ as a function of temperature for H₂O and D₂O.

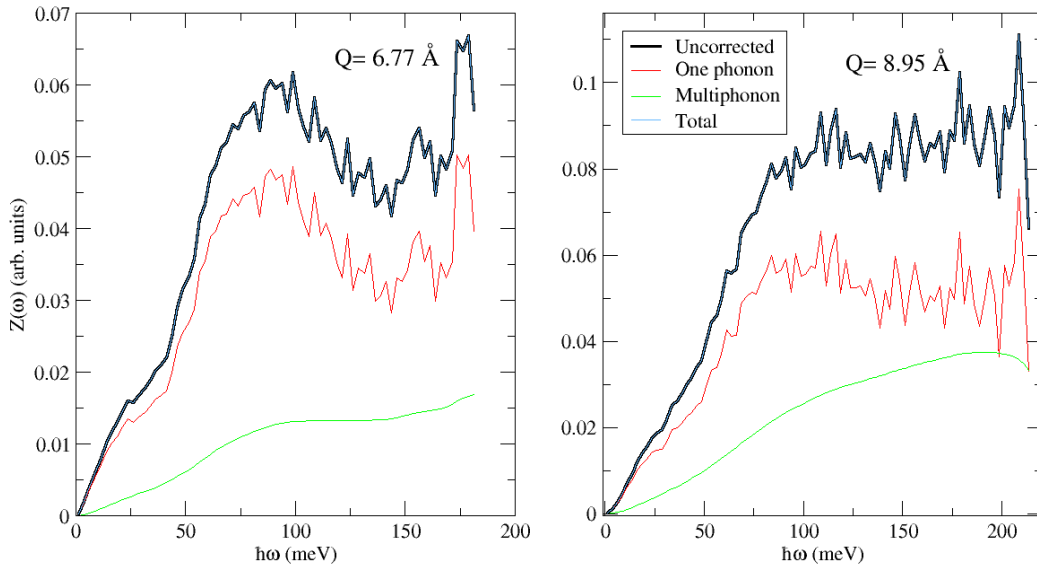


Figure 4. Detail of the calculated single and multi-phonon components, for the light water sample at 300 K, and $Q = 6.77 \text{ \AA}^{-1}$ and $Q = 8.95 \text{ \AA}^{-1}$, after the convergence of the iterative correction process.

In Fig. 4 we show the detail of the single and multi-phonon components for the spectra of water at 300 K (previously corrected by multiple-scattering effects), compared with the uncorrected data. The spectra were multiplied by the factor $\frac{\omega}{n(\omega)+1}$ so the resulting single-phonon component is directly comparable to $Z(\omega)$. The total calculated scattering coincides with the original raw data, thus showing the good convergence of the method.

5. Results

In Fig. 5 we show the final densities of states obtained after the multiple scattering and multi-phonon corrections described in this work. The Q -range chosen to average $Z(Q, \omega)$ was from 2 \AA^{-1} to 7.6 \AA^{-1} , with the criterion of employing values of Q where a reasonable ω -range is accessible, while multi-phonon corrections are not excessive.

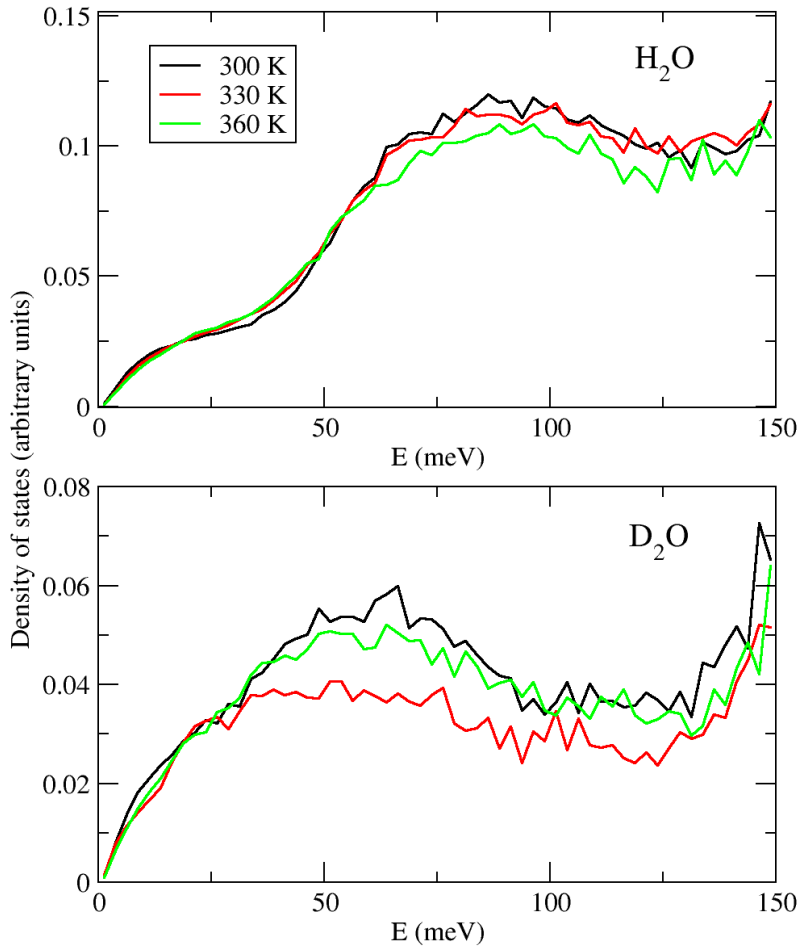


Figure 5. Densities of states of H₂O and D₂O at different temperatures obtained after the procedure described in this work.

6. Conclusions

We have studied the densities of states of H₂O and D₂O at different temperatures, with inelastic neutron scattering experiments. The process process to treat the experimental data involves *ad-hoc* developments to calculate multiple scattering and multi-phonon contributions to the experimental spectra.

The energy-range studied, corresponds to collective molecular motions. The results show slight variations of $Z(\omega)$ in the selected temperature range, with a maximum about 90 meV

for H₂O and 60 meV for D₂O. The results differ with Bellissent's [8], especially in the low-frequencies domain. In our experiment the energy resolution is broader than the feature present at that region, what prevents us to observe its detail.

The next steps in this research program involve the calculation of cross sections employing the densities of states of this work. Also an experimental study in the low-energies range (0 to 20 meV) with a higher resolution spectrometer is desirable to improve the knowledge of collective dynamics.

Acknowledgments

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