The inelasticity correction for liquid water in neutron scattering

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Abstract. In this paper, we show that an empirical method using a polynomial expansion allows us to perform a reliable inelasticity correction for liquid water studied by neutron diffraction, at three different wavelengths. A unique liquid structure factor has been deduced, even in the case of the mixture D_2O/H_2O (10% wt), and the parameters of the water molecule determined.

1. Introduction

The precise determination of the partial pair correlation functions for liquid water has remained an important goal of liquid state physics for the last decade. Although several groups have made important developments in difficult measurements using the H/D substitution in conjunction with neutron diffraction studies, a definitive solution to this problem has not yet been achieved. During this period there have also been substantial improvements in beam intensity and instrumentation and it has become desirable to repeat some of the earlier experiments with improved statistical accuracy. In this paper, we return to the basic study of liquid D_2O at room temperature and reexamine the details of the inelasticity corrections in relation to the structural information extracted from the intra- and intermolecular components.

The detailed description of neutron scattering by an assembly of D_2O molecules is complicated by a number of factors due to inelasticity effects, which are broadly classed under the title 'Placzek corrections', and several groups [1–6] have worked on this topic in an effort to determine the corrections *ab initio*.

For the analysis of the present data obtained at various wavelengths, we use an empirical method described in earlier papers on liquid DF [7], high-density amorphous ice [8] and, more recently, on ND_3 [9]. The inelasticity correction obtained is compared with some of the previously mentioned corrections. To check the validity of such a procedure the method is also applied to a D_2O/H_2O (10% wt) mixture.

2. Formalism

The differential scattering cross section for scattering of neutrons by an assembly of fixed nuclei (forming molecules or not) is given in the static approximation by [10]:

$$\frac{d\sigma}{d\Omega} = \left\langle \sum_{ij} b_i b_j \exp(iQ \cdot r_{ij}) \right\rangle + \sum_{ij} \frac{\sigma_j}{4\pi} \delta_{ij} \qquad (1)$$

where b_i, b_j are the coherent scattering lengths and σ_j the incoherent scattering cross sections. This cross section may be split into a self-part ($i = j$) and a distinct part:

$$d\sigma/d\Omega = (d\sigma/d\Omega)^{self} + (d\sigma/d\Omega)^{distinct}. \qquad (2)$$

The self-part itself can be split into an incoherent and a self-coherent part:

$$(d\sigma/d\Omega)^{self} = (d\sigma/d\Omega)_{coh}^{self} + (d\sigma/d\Omega)_{incoh}^{self}. \qquad (3)$$

In the case of pure D_2O:

$$(d\sigma/d\Omega)^{self} = (b_O^2 + 2b_D^2) + 2\sigma_i^D/4\pi \qquad (4)$$

where b_O and b_D are the coherent scattering lengths relative to oxygen and deuterium atoms, $b_O = 0.5805 \times 10^{-12}$ cm, $b_D = 0.6674 \times 10^{-12}$ cm, and where $\sigma_i^D = 2.032$ b is the incoherent scattering cross section due to deuterium atoms D (the incoherent cross section of oxygen is zero).

The distinct part can be separated into intra- and intermolecular parts corresponding to correlations between atoms within the same molecule and atoms belonging to different molecules, respectively:

$$(d\sigma/d\Omega)^{distinct} = (d\sigma/d\Omega)^{intra} + (d\sigma/d\Omega)^{inter}. \qquad (5)$$

The differential scattering cross section may thus be expressed by the relation:

$$d\sigma/d\Omega = (d\sigma/d\Omega)^{self} + (d\sigma/d\Omega)^{intra} + (d\sigma/d\Omega)^{inter}. \qquad (6)$$

The liquid structure factor $S_M(Q)$ is defined from the distinct part of the differential scattering cross section; for liquid D_2O, it is given by:

$$S_M(Q) = [(d\sigma/d\Omega)^{distinct} + b_O^2 + 2b_D^2]/(b_O + 2b_D)^2 \qquad (7)$$

where Q is the scattering wavevector.

For a molecular liquid, the structure factor may be split into two parts:

$$S_M(Q) = f_1(Q) + D_M(Q). \qquad (8)$$

$f_1(Q)$ is the molecular form factor and the $D_M(Q)$ function contains all the intermolecular contributions.

At very large Q-values, $D_M(Q)$ goes to zero. Then, the main contribution to the structure factor comes from $f_1(Q)$. However, for hydrogen-bonded liquids, the intermolecular contribution $(d\sigma/d\Omega)^{inter}$ can be observed at high values of Q [11], and so it is difficult to define the low limit of Q from which this property becomes valid.

The total pair correlation function $g(r)$ is related to the Fourier transform of $S_M(Q)$ by the relation

$$4\pi r\rho_M(g(r) - 1) = \frac{2}{\pi} \int_0^\infty Q(S_M(Q) - S_M(\infty)) \sin Qr \, dQ \qquad (9)$$

where $S_M(\infty) = (b_O^2 + 2b_D^2)/(b_O + 2b_D)^2$ is the asymptotic value of $f_1(Q)$ at large Q and ρ_M is the molecular number density.

The function $g(r)$ is a combination of the different partial correlation functions and includes both the intermolecular and intramolecular distances. It is more convenient to remove the intramolecular terms by subtracting the molecular form factor from $S_M(Q)$ to
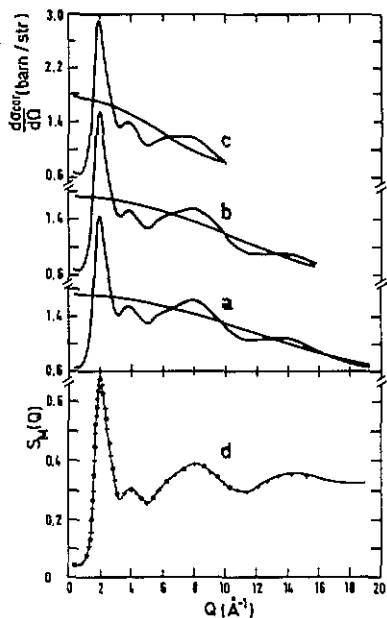
Figure 1. Differential neutron scattering cross sections $d\sigma^{cor}(Q)/d\Omega$ for liquid D_2O at 27 °C at three incident wavelengths, 0.587 Å (curve a), 0.712 Å (curve b) and 1.116 Å (curve c). The full monotonic curves are the self-scattering cross sections $P(Q)$ calculated using a polynomial expansion. The lower curve (d) gives the structure factor $S_M(Q)$ for liquid D_2O and shows good agreement after correction between the data obtained at the three wavelengths: (the accuracy is estimated to be about 1%) $-$, 0.587 Å; $+$, 0.712 Å; $\bullet$, 1.116 Å.

obtain $D_M(Q)$, which may be Fourier transformed in order to obtain the pair correlation function $g_L(r)$ for the intermolecular terms only:

$$4\pi r \rho_M (g_L(r) - 1) = \frac{2}{\pi} \int_0^\infty Q D_M(Q) \sin Qr \, dQ. \tag{10}$$

In this way, no truncation effect arises; moreover, the first peaks due to the intramolecular distances disappear in the low-r range. This property will be used to adjust the flexible parameters in section 4.2.

3. Experimental procedure and data treatment

The experiments were performed at the reactor Orphée, at the Laboratoire Léon Brillouin, on the 7C2 spectrometer [12] which is equipped with a BF_3 position-sensitive detector with 640 cells. The angular step between two adjacent cells is equal to 0.2° which leads to a maximum diffraction angle 2θ of 128°. The three incident wavelengths used $\lambda_0 = 1.116$ Å, 0.712 Å and 0.587 Å allowed us to cover a range of scattering wave vectors ($Q = 4\pi \sin \theta / \lambda_0$) extending from 0.35 Å^{-1} to 19 Å^{-1}. Liquid D_2O was obtained from CEA-ORIS with an enrichment of 99.95% deuterium. The D_2O sample and the (D_2O–10% H_2O) mixture were held in containers of thin-walled vanadium (0.1 mm thick) with internal diameters respectively equal to 8 mm and 6 mm.

The usual measurements of 'sample + container', 'empty container', standard 'vanadium bar' and 'background' were made. After the usual experimental corrections for container scattering, sample attenuation and multiple scattering had been applied, the absolute differential scattering cross sections for liquid D_2O and for the D_2O–H_2O 10% mixture at 27 °C were evaluated. The wavelength and detector zero-angle were obtained from standard calibration measurements using a nickel powder. Figure 1 shows the differential scattering cross sections $d\sigma_{cor}/d\Omega$ of D_2O, measured at three wavelengths.

4. Inelasticity correction

The measured differential scattering cross section in a reactor experiment is given, at constant angle 2θ, and for an incident wavelength λ_0 by:

$$\frac{d\sigma}{d\Omega}(2\theta, \lambda_0) = \int_{-\infty}^{\omega_0} d\omega \, \varepsilon(k_s)(k_s/k_0)S_M(Q, \omega) \tag{11}$$

where k_0 and k_s are the momentum of incident and scattered neutrons, respectively. Q is the momentum transfer: $Q = k_s - k_0$.

The energy of the scattered neutron is shifted by an amount $\hbar\omega$ (where $\hbar$ is Planck's constant) from the incident energy due to recoil of the scatterer and other inelastic collision effects:

$$\hbar\omega = (\hbar^2/2m)(k_s^2 - k_0^2). \tag{12}$$

$S_M(Q, \omega)$ is the frequency-dependent inelastic scattering function:

$$S_M(Q, \omega) = \sum_{i,j} \left(b_i b_j + \frac{\sigma_j}{4\pi}\delta_{ij}\right)S_{ij}(Q, \omega) \tag{13}$$

with summation over all atoms i, j in the system. One has:

$$S_M(Q) = \int_{-\infty}^{+\infty} S_M(Q, \omega) \, d\omega. \tag{14}$$

The inelasticity correction is due to the difference between the energy-integrated intensity at constant angle (equation (11)) and the static scattering function $S_M(Q)$ (equation (14)):

$$\Delta(2\theta, \lambda_0) = (d\sigma/d\Omega)(2\theta, \lambda_0) - \varepsilon(k_0)S_M(Q). \tag{15}$$

The detector sensitivity function is $\varepsilon(k_s) = 1 - e^{-\alpha/k_s}$; for the detector used in the experiments, $\alpha = 1.765 \, \text{Å}^{-1}$ and $\varepsilon(k_0) = \varepsilon_0$.

4.1. Empirical method

4.1.1. Correction of the self-scattering cross section. For low-mass-atom materials, the evaluation of the self-term (equations (3), (4)) including coherent and incoherent contributions is strongly affected by inelastic processes and leads to a steady fall-off in the overall intensity as 2θ (or Q) is increased (see figure 1(a), (b), (c)). Thus, following the Placzek formalism [13], the self-term can be expressed by means of a power series expansion which may be approximated by a polynomial expansion [9], such that:

$$[(d\sigma/d\Omega)(2\theta, \lambda_0)]^{self} = P(2\theta, \lambda_0)$$

where

$$P(2\theta, \lambda_0) = A + BQ^2 + CQ^4 + DQ^6. \tag{16}$$

The coefficient D is very small and has a slight effect just for large Q [9]; we do not take it into account, because our maximum Q-value is smaller than 20 Å^{-1}. The differential scattering cross section (equation (2)) is then expressed as:

$$(d\sigma/d\Omega)(2\theta, \lambda_0) = P(2\theta, \lambda_0) + (d\sigma/d\Omega)^{dist}(2\theta, \lambda_0). \tag{17}$$

4.1.2. Recoil corrections. For molecules containing light atoms such as water, the distinct

term must be corrected for recoil, particularly when the molecules are allowed to move, as is the case for liquids. If Q_{eff} is the actual momentum transfer modulus, one may write, after Walford *et al* [14]:

$$\left(\frac{Q_{eff}}{Q}\right)^2 = \frac{1 + C_E^2(\theta) - 2C_E(\theta)\cos 2\theta}{2(1 - \cos 2\theta)} \tag{18}$$

with

$$C_E(\theta) = [m_n/(M_{eff}^r + m_n)] \{\cos 2\theta + [(M_{eff}^r/m_n)^2 - \sin^2 2\theta]^{1/2}\}$$

where M_{eff}^r is a recoil effective mass close to the mass of the molecule for liquids or gases and m_n is the neutron mass.

4.1.3. Differential scattering cross section for D_2O. The D_M function (equation (8)) can then be expressed, in the case of D_2O, by:

$$\begin{aligned}
D_M(Q) = \{&(1/K)I_{cor}(Q) - A - BQ^2 - CQ^4 + b_O^2 + 2b_D^2 \\
&- [b_O^2 + 2b_D^2 + 4b_O b_D j_0(Q_{eff}r_{OD})\exp(-\gamma_{OD}Q_{eff}^2) \\
&+ 2b_D^2 j_0(Q_{eff}r_{DD})\exp(-\gamma_{DD}Q_{eff}^2)]\}/(b_O + 2b_D)^2
\end{aligned} \tag{19}$$

where I_{cor} is the intensity corrected for container scattering, sample attenuation and multiple scattering, K is the normalization factor, r_{OD} is the intramolecular oxygen–deuterium distance and $r_{DD} = 2r_{OD}\sin(\frac{1}{2}\beta)$ for an intramolecular bond angle β, $j_0(x) = (\sin x/x)$ is the zeroth-order spherical Bessel function and $\gamma_{ij} = \frac{1}{2}\langle u_{ij}^2\rangle$ where $\langle u_{ij}^2\rangle$ is the mean square amplitude of the displacement from the equilibrium position due to the normal mode of vibration of the molecule.

As previously mentioned, we took advantage of the fact that the Fourier transform of D_M cannot exhibit oscillations in the low-r region to adjust the various parameters; by minimizing the oscillations of $g_L(r)$ in the r-range between 0 and 1.6 Å, at the smallest wavelength ($\lambda_0 = 0.587$ Å), we first adjusted the parameters B and C, keeping the other parameters in (19) fixed. K is experimentally known and A—roughly equal to $b_O^2 + 2b_D^2 + 2\sigma_i^D/4\pi$, see below—is connected to K via the isothermal compressibility χ_T by the relation

$$S_M(0) = \rho_M k_B T\chi_T = [(1/K)I_{cor}(0) - A + b_O^2 + 2b_D^2]/(b_O + 2b_D)^2. \tag{20}$$

The values of the parameters related to the molecule, say r_{OD}, r_{DD}, γ_{OD}, γ_{DD}, are taken equal to those in the vapour phase in the first step of the refinement. The second step consisted of leaving M_{eff}^r and the parameters of the molecule free, and again minimizing the oscillations. Finally all the parameters, including A and K, were submitted to refinement. This procedure allowed us to take into account an eventual residual multiple-scattering effect if this last correction was not accurately estimated.

Figure 2 (curve a) shows the Q-weighted D_M function finally obtained and the corresponding $g_L(r)$ function (curve b). The values of $D_M(Q)$ are given in table 1. Although $QD_M(Q)$ seems to exhibit oscillations at about 19 Å^{-1}, this does not affect the procedure adopted: we have verified this assertion by multiplying $QD_M(Q)$ by a damping function. In both cases, the constants A, B, C, K have been found to be identical. We found an intramolecular oxygen–deuteron distance equal to 0.989 Å and a deuteron–deuteron distance equal to 1.583 Å ($\beta = 106.3°$) with $\gamma_{OD} = 1.72 \times 10^{-3}$ Å^2 and $\gamma_{DD} = 3.75 \times 10^{-3}$ Å^2.
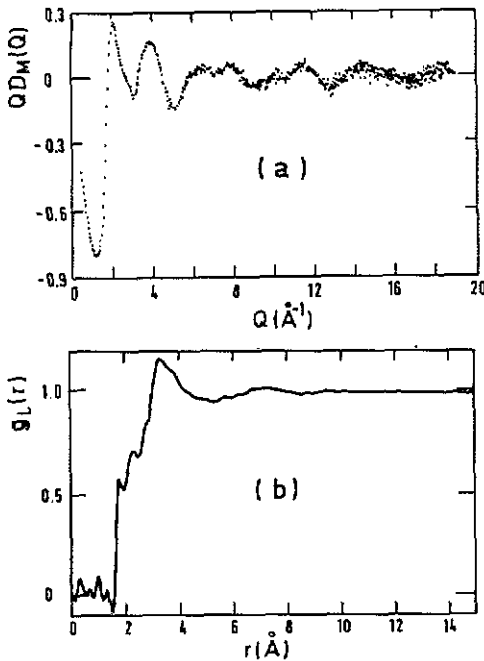
Figure 2. (a) The $QD_M(Q)$ function for liquid D_2O at 27 °C. (b) The pair correlation function $g_L(r)$ for liquid D_2O at 27 °C.
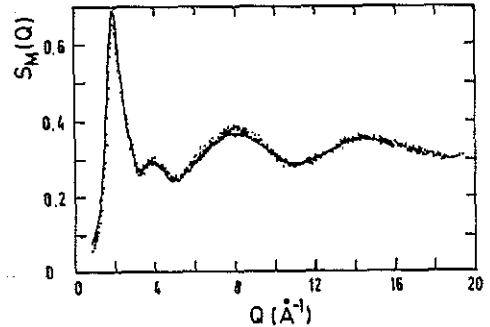

Figure 3. The structure factor $S_M(Q)$ for a D_2O/H_2O (10% wt) mixture, at 27 °C. Notice the good agreement after correction between the data obtained at two wavelengths: dots, 0.577 Å; —, 0.7045 Å.

The same kind of adjustment was applied to the D_2O/H_2O (10% wt) mixture.

Table 2 gives the values of the parameters for D_2O, at the three different wavelengths, and for D_2O/H_2O mixture at two wavelengths.

As noted in [9], a first expansion of (17) leads to the expression

$$Q_{eff} = Q[1 - (m_n/M'_{eff})(\lambda_0/4\pi)^2 Q^2]. \tag{21}$$

The ratio λ_0^2/M'_{eff}, related to the recoil effect and calculated from the data given in table 2, is found to be nearly constant either for pure D_2O or for the mixture. Hence the $S_M(Q)$ functions can be compared on the same graph: the liquid structure factors relative to D_2O and the D_2O/H_2O (10% wt) mixture are given in figures 1(d) and 3.

For each sample there is a very good agreement after correction between the data obtained at different wavelengths, as shown by the good overlap between the points. Although this method for correcting inelasticity effects is an empirical one, it has the merit of leading to a unique structure factor even in the case of the mixture D_2O/H_2O where the hydrogen content (10% wt) is important. This last measurement was performed only to check the method; the statistics was poor which explains the difference between the two curves obtained at the two different wavelengths. Further precise measurements have been done in order to extract the partial structure factors of water. Moreover, the method can correct some defects in the experimental data reduction providing that the corrections are monotonic functions of Q.

4.2. Comparison with previous published inelasticity corrections

In order to compare our results concerning the inelasticity corrections with those deduced from well known methods, we have found in each case, for a given wavelength,

Table 1. The intermolecular function $D_M(Q)$ of liquid D_2O at 27 °C (the data given in brackets are data interpolated between the value calculated at $Q = 0$ and the first experimental value).

Q	D_M	Q	D_M	Q	D_M	Q	D_M	Q	D_M
(0.0	−0.936 00)	3.9	0.041 62	7.8	0.006 11	11.7	0.003 81	15.6	0.000 17
(0.1	−0.941 31)	4.0	0.039 28	7.9	0.006 46	11.8	0.003 20	15.7	0.000 07
(0.2	−0.941 31)	4.1	0.035 17	8.0	0.006 32	11.9	0.002 69	15.8	−0.000 07
(0.3	−0.934 96)	4.2	0.028 56	8.1	0.005 08	12.0	0.001 81	15.9	−0.000 25
0.4	−0.927 02	4.3	0.020 53	8.2	0.004 09	12.1	0.000 90	16.0	−0.000 41
0.5	−0.917 58	4.4	0.011 46	8.3	0.002 57	12.2	0.000 17	16.1	−0.000 64
0.6	−0.896 89	4.5	0.002 55	8.4	0.001 28	12.3	−0.001 12	16.2	−0.000 63
0.7	−0.872 82	4.6	−0.006 26	8.5	−0.000 40	12.4	−0.002 04	16.3	−0.000 92
0.8	−0.844 21	4.7	−0.014 23	8.6	−0.001 91	12.5	−0.002 94	16.4	−0.001 18
0.9	−0.811 19	4.8	−0.020 67	8.7	−0.003 00	12.6	−0.003 79	16.5	−0.001 41
1.0	−0.770 27	4.9	−0.025 02	8.8	−0.004 01	12.7	−0.004 37	16.6	−0.001 51
1.1	−0.722 32	5.0	−0.027 34	8.9	−0.004 61	12.8	−0.004 36	16.7	−0.001 47
1.2	−0.667 02	5.1	−0.027 70	9.0	−0.005 19	12.9	−0.004 21	16.8	−0.001 59
1.3	−0.602 00	5.2	−0.025 74	9.1	−0.004 76	13.0	−0.003 76	16.9	−0.001 71
1.4	−0.519 71	5.3	−0.022 32	9.2	−0.004 51	13.1	−0.003 07	17.0	−0.001 85
1.5	−0.420 66	5.4	−0.018 29	9.3	−0.004 33	13.2	−0.002 75	17.1	−0.001 69
1.6	−0.304 86	5.5	−0.013 28	9.4	−0.004 25	13.3	−0.002 08	17.2	−0.001 42
1.7	−0.171 54	5.6	−0.008 53	9.5	−0.004 16	13.4	−0.001 74	17.3	−0.001 24
1.8	−0.031 63	5.7	−0.004 76	9.6	−0.003 69	13.5	−0.001 11	17.4	−0.000 93
1.9	0.073 00	5.8	−0.001 74	9.7	−0.003 27	13.6	−0.000 63	17.5	−0.000 57
2.0	0.123 51	5.9	0.000 44	9.8	−0.002 64	13.7	−0.000 17	17.6	−0.000 16
2.1	0.118 96	6.0	0.002 17	9.9	−0.002 06	13.8	0.000 40	17.7	−0.000 02
2.2	0.096 01	6.1	0.003 29	10.0	−0.001 29	13.9	0.001 05	17.8	0.000 04
2.3	0.065 25	6.2	0.003 91	10.1	−0.000 18	14.0	0.001 53	17.9	0.000 26
2.4	0.042 77	6.3	0.004 32	10.2	0.000 10	14.1	0.001 79	18.0	0.000 47
2.5	0.026 19	6.4	0.004 54	10.3	−0.000 08	14.2	0.002 21	18.1	0.000 62
2.6	0.013 85	6.5	0.004 79	10.4	−0.000 39	14.3	0.002 10	18.2	0.000 73
2.7	0.004 07	6.6	0.005 11	10.5	−0.000 67	14.4	0.002 48	18.3	0.000 91
2.8	−0.003 65	6.7	0.004 77	10.6	−0.000 68	14.5	0.002 30	18.4	0.001 21
2.9	−0.015 78	6.8	0.003 91	10.7	−0.000 73	14.6	0.001 94	18.5	0.001 53
3.0	−0.025 52	6.9	0.003 42	10.8	−0.000 35	14.7	0.001 70	18.6	0.001 45
3.1	−0.026 38	7.0	0.002 86	10.9	0.000 56	14.8	0.001 45	18.7	0.001 28
3.2	−0.016 26	7.1	0.002 55	11.0	0.001 58	14.9	0.001 26	18.8	0.001 33
3.3	−0.001 58	7.2	0.002 17	11.1	0.002 50	15.0	0.000 93	18.9	0.000 98
3.4	0.011 76	7.3	0.002 01	11.2	0.003 30	15.1	0.000 87	19.0	0.000 34
3.5	0.023 08	7.4	0.002 63	11.3	0.003 97	15.2	0.000 84	0.0	0.000 00
3.6	0.031 37	7.5	0.003 83	11.4	0.004 31	15.3	0.000 69	0.0	0.000 00
3.7	0.038 32	7.6	0.004 56	11.5	0.004 30	15.4	0.000 58	0.0	0.000 00
3.8	0.041 29	7.7	0.005 50	11.6	0.004 16	15.5	0.000 32	0.0	0.000 00

the ratio between the polynomial expansion $P(Q)$ and the calculated self-cross section $(d\sigma^{calc}/d\Omega)^{self}$; in figure 4 the results relating to the method of Powles [1, 15] and the synthetic model of Granada *et al* [5, 6] are given.

It appears that the better agreement with the empirical method is obtained with the synthetic model of Granada *et al*. A nearly constant value of the ratio (see figure 4) is found for the shortest wavelengths for which the determination of the $P(Q)$ polynomial expansion is the more reliable. For $\lambda = 1.116$ Å, a more serious disagreement exists, but in this case we have assumed that a parabolic function can describe fairly adequately a strongly varying function. The departure of the ratio from the value 1 can have several origins. The constant A includes the total self-scattering cross section (1.551 b sr^{-1}), the

Table 2. Parameters A, B, C of $P(Q)$ and recoil effective mass M'_{eff} as functions of the incident wavelength for D_2O and the mixture D_2O/H_2O (10% wt), at 27 °C (1 b = 10^{-24} cm²).

	$\lambda_0(\text{Å})$	A (b sr⁻¹)	B (b sr⁻¹ Å²)	C (b sr⁻¹ Å⁴)	M'_{eff}
D_2O	0.587	1.724	-4.5968×10^{-3}	4.9024×10^{-6}	12.5
	0.712	1.736	-6.2271×10^{-3}	8.6224×10^{-6}	13.1
	1.116	1.75	-1.657×10^{-2}	7.349×10^{-5}	31.8
$D_2O + H_2O$ (10% wt)	0.577	2.905	-1.2631×10^{-2}	1.6772×10^{-5}	9.9
	0.7045	2.911	-1.6351×10^{-2}	3.0351×10^{-5}	13.8

rotations of the molecule (not taken into account in the synthetic model of Granada *et al* [5, 6]) and eventually some residual multiple-scattering correction.

Some further checking of the validity of the polynomial expansion procedure has been done by calculating the moments $\langle\omega^2\rangle'$ of liquid D_2O following a method suggested by Blum *et al* [2, 3]. At small angles, the inelasticity correction $\Delta(\theta)$ can be expressed in terms of the derivatives of the frequency moments of the dynamical structure factor of a fluid, $\langle\omega^2\rangle'$, $\langle\omega^3\rangle'$ and $\langle\omega^4\rangle'$:

$$\Delta(0) = (\varepsilon_0/v_0^2)\langle\omega^2\rangle' + (1/v_0^3)(\varepsilon_0/k_0 - \varepsilon_1)\langle\omega^3\rangle' + (\varepsilon_0/v_0^4)\langle\omega^4\rangle' + \dots \tag{22}$$

The self-differential scattering cross section is written as:

$$\left(\frac{d\sigma}{d\Omega}(2\theta, \lambda_0)\right)^{\text{self}} = \Delta(2\theta, \lambda_0) + \left(\sum_{ij} b_i b_j + \frac{\sigma_j}{4\pi}\delta_{ij}\right) \tag{23}$$

At the small-angle limit, and for liquid D_2O, it becomes:

$$[(d\sigma/d\Omega)(0, \lambda_0)]^{\text{self}} = \Delta(0, \lambda_0) + 1.551 = A \tag{24}$$

where $[(d\sigma/d\Omega)(0, \lambda_0)]^{\text{self}}$ can be approximated by the A-parameter of the polynomial expansion. Table 3 gives the values of $(d\sigma/d\Omega)(0)$ and those of the zero-angle correction $\Delta(0)/\varepsilon_0$ as a function of the incident wavelength λ_0 (or $k_0 = 2\pi/\lambda_0$).

Thus we can write:

$$\Delta(0)/\varepsilon_0 = (1/v_0^2)\langle\omega^2\rangle' + (1/v_0^3)(1/k_0 - \varepsilon_1/\varepsilon_0)\langle\omega^3\rangle' + (1/v_0^4)\langle\omega^4\rangle' + \dots \tag{25}$$

First, we have assumed that

$$\Delta(0)/\varepsilon_0 \simeq (1/v_0^2)\langle\omega^2\rangle' \tag{26}$$

so, using the relation $1/v_0 = m_n/\hbar k_0$, equation (26) becomes:

$$\Delta(0)/\varepsilon_0 \simeq (m_n^2/\hbar^2)\langle\omega^2\rangle'/k_0^2. \tag{27}$$

In figure 5, we have plotted $\Delta(0)/\varepsilon_0$ against k_0^{-2} together with the theoretical curve (equation (27)) evaluated from the first derivative of the frequency moments of classical rigid rotators, $\langle\omega^2\rangle' = A_s + A_d$ where $A_s = 89.77$ b Å² ps⁻² is the self-part and $A_d = -1.1378$ b Å² ps⁻² is the distinct part [3]. There is some departure from the theoretical behaviour, which is more pronounced at the larger wavelength where the uncertainties
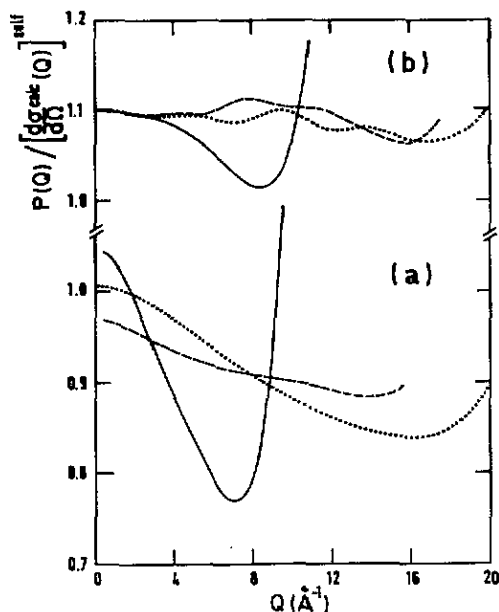
Figure 4. (a) The ratio between $P(Q)$ and $(d\sigma^{calc}(Q)/d\Omega)^{self}$. The method of Powles [1, 15] has been used for the calculation ($\cdots$, 0.577 Å; $---$, 0.709 Å; ——, 1.112 Å). (b) The ratio between $P(Q)$ and $(d\sigma^{calc}(Q)/d\Omega)^{self}$. The calculated self-cross section is deduced from the synthetic model of Granada [5, 6] ($\cdots$, 0.587 Å; $---$, 0.712 Å; ——, 1.116 Å).
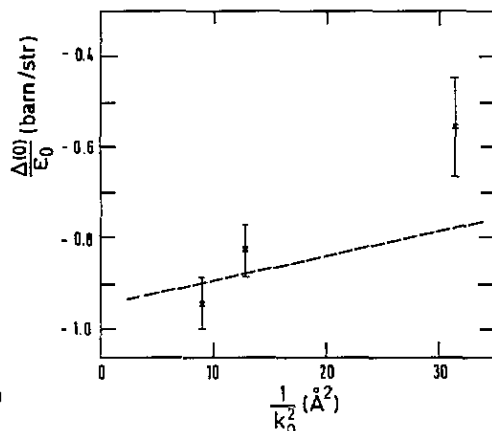
Figure 5. The zero-angle correction $\Delta(0)/\varepsilon_0$ versus k_0^{-2}. ×: experimental points. The broken line has the theoretical slope proportional to the first derivative of the frequency moments of classical rigid rotators given by $\langle\omega^2\rangle' = A_s + A_d$ with $A_s = 89.77$ b Å^{2}ps^{-2} and $A_d = -1.1378$ b Å^{2}ps^{-2} [2, 3]. The error bars correspond to a precision of 0.5% and 1% in the determination of A, respectively at the two shorter wavelengths and at 1.116 Å.

Table 3. The self-scattering cross section ($2\theta = 0$) and zero-angle correction as functions of the incident wavelength, for D_2O at 27 °C (1 b = 10^{-24} cm^2).

λ_0 (Å)	k_0 (Å^{-1})	ε_0	$[(d\sigma/d\Omega)(0)]^{self}$ (b sr^{-1})	$\Delta(0)/\varepsilon_0$ (b sr^{-1})
1.116	5.630	−0.368	1.724	−0.54
0.712	8.825	−0.221	1.736	−0.837
0.587	10.704	−0.179	1.75	−0.966

in the parameters of $P(Q)$ are larger. However, experiments at other wavelengths would be necessary in order to make a more precise comparison with the model of Blum *et al* [3].

5. Conclusion

In this paper, we have shown that an empirical method is reliable for making corrections for the recoil and inelasticity effects in the case of neutron scattering by water. This method is based on a polynomial expansion of the self-differential scattering cross section and includes recoil effect corrections; it has been successful in the case of a $D_2O/$

H_2O mixture and, in the near future, it will be used in order to determine the pair partial functions for liquid water at various temperatures and at high pressures.

In order to test this empirical method differently, we have attempted to use a neutron pulsed source. Experiments have been performed on D_2O at 27 °C on the LAD at ISIS (Rutherford Appleton Laboratory). By taking into account the data provided by the counters set in the small-angle range (that is, in the case where the inelastic effects are smallest), we have compared the data obtained from the two kinds of neutron source facility. Roughly, the results are in good agreement, but the very poor statistics and also the recoil effect in the pulsed neutron measurements prevented us from placing much reliance on this comparison.

Acknowledgments

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