Cross Section Model and Scattering Law of Liquid Water for Design of a Cold Neutron Source

Yoshinobu EDURA[1], Seiji TASAKI and Nobuhiro MORISHIMA

Department of Nuclear Engineering, Kyoto University,
Yoshida, Sakyo-ku, Kyoto 606-8501, Japan
E-mail: edura@nucleng.kyoto-u.ac.jp

Abstract: A cross section model for cold neutron scattering in light water is developed, which describes various molecular motions inherent to hydrogen-bonded water molecules especially in terms of jump- and rotational-diffusion processes. Inter- and intra-molecular vibrations are also included. A systematic analysis is performed of a velocity autocorrelation function, a generalized frequency distribution and double-differential and total cross sections. Good agreement with the results of computer molecular dynamics and neutron scattering experiments is found. A wide range of cross section evaluation for neutron energies from 0.1 μeV to 10 eV and liquid temperatures between the melting and boiling points is performed. This permits us to generate such low-energy neutron cross section libraries as group constants set and scattering law for ultra-cold, very-cold, cold and thermal neutrons. Together with the libraries for liquid ^{4}He, H_2, D_2 and solid and liquid CH_4, a powerful tool for design of an advanced low-energy neutron source is now ready for use.
Keywords: Light water, Molecular dynamics, Cross section, Scattering law, Cold neutron, Thermal neutron, Neutron source.

1 Introduction

Cold ($\sim$ 1 meV) and thermal ($\sim$ 25 meV) neutrons are expected to be useful in studying microscopic structures and molecular dynamics of various materials such as soft condensed matters, bio-molecules, super-conductors and industrial products. To utilize these neutrons actually, a spallation neutron source is being constructed in Japan, USA and Europe. High-energy (~MeV) neutrons generated from a spallation target must be moderated to thermal and cold neutrons with an optimized hydrogenous material like light water (H_2O), liquid H_2 and solid CH_4. Hence neutronic properties of such moderators need to be studied especially in terms of scattering and slowing-down processes. The present paper is devoted in this direction. A cross section model for neutron scattering in liquid water is devolped, which is applicable to a wide range of incident neutron energy from 0.1 μeV (ultra-cold) to 10 eV (epi-thermal) and all practical temperatures between melting and boiling points.

Another purpose of the present paper is to describe water-molecule dynamics in terms of hydrogen-bonding properties and related various relaxation processes on the molecular translations and rotations

[1] Corresponding author.

in a wide time scale from ~0.001 to ~100 ps. A set of characterizing functions such as a velocity auto-correlation function, an intermediate scattering function and a dynamical scattering law is systematically calculated. These are necessary for a physical and unified interpretation of neutron-scattering and molecular-dynamics results.

In Sec. 2, a brief description is given of the double-differential cross section model of light water. Sec. 3 discusses many cross-section results, both double-differential and total, by comparison with available experimental results at various practical temperatures. Sec. 4 is devoted to the generation of group-constants set and scattering law. Some concluding remarks are given in Sec. 5.

2 Cross Section Model

The physical properties of liquid water are especially anomalous at low temperatures, for instance, as is the case with H_2O showing the maximum density at 4 °C, the minimum isothermal compressibility at 46 °C, non-Arrhenius behavior of the self-diffusion coefficient, and so on. For this complexity of water, a theoretical model of water dynamics remains to be developed. On the other hand, recent scattering experiments with light, X-ray and neutron are being characterizing the structure and dynamics of water at the microscopic level. In particular, neutron scattering is applied to study the translational and rotational motions of water molecules in the hydrogen-bond network with a finite lifetime. More recently, computer molecular-dynamics simulations have served for the interpretation of experimental results in terms of effective potentials of water molecule and various transport properties of liquid water.

The present paper aims at developing an accurate model of water based on the newly available experimental data and computer simulation results. The main object is twofold, i.e. to interpret systematically the data in an energy-momentum domain and the results in a space-time domain, and to generate a cross-section library for design of a low-energy neutron source. This requires the model to be capable of quantitative treatment in a wide range of the above-mentioned domain. At present, attention is paid to light water (H_2O) as an incoherent scatter showing individual motions of water molecule. The following features for molecule dynamics are taken into account:

- A water molecule is hindered in translational motion by a hydrogen-bond network formed intermittently with an average residence time having strong temperature dependence.
- Translational diffusion and vibration are repeated as a jump diffusion process [1]. The former is characterized with the self-diffusion constant at given temperature, while the latter vibration is due to an intermolecular motion with bending and stretching modes.
- Rotational motions of molecule are consisting of two parts, i.e. a rotational diffusion process with a large relaxation (reorientational) time having an Arrhenius behavior [2], and a hindered rotation with the librational band centered around 65 meV on account of intermolecular coupling with surrounding molecules.
- Intramolecular vibrations with bending, stretching and asymmetric stretching modes are also included.
- These motions tend to behave as free gases of H and O at a very-short time scale of, say, 0.001 ps, which is required to reproduce a free-atom cross section for an epithermal neutron.

All these dynamics are described in an explicit form by a velocity auto-correlation function $\phi(t)$ and, equivalently, a generalized frequency distribution function $D(\omega)$. Their changes in liquid temperature are involved with translational and rotational diffusion coefficients, a residence time, a reorientational time and so on. Once $\phi(t)$ or $D(\omega)$ has been constructed, a space-time density correlation function $G_s(r,t)$ for individual motions can be obtained readily by the Gaussian approximation. Also the analytical Fourier transform of $G_s(r,t)$ with respect to r yields an intermediate scattering function

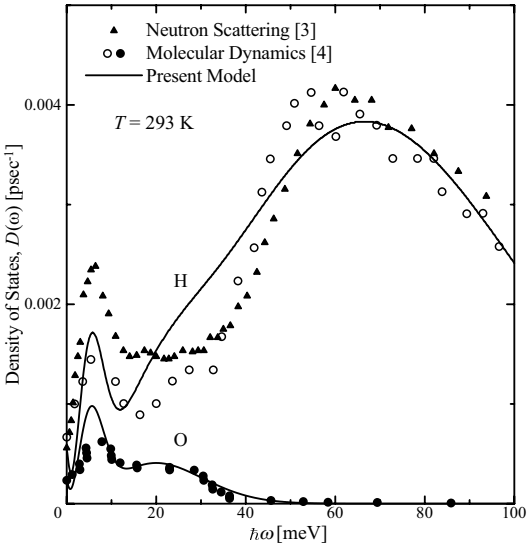

Fig. 1: Behavior of $D(\omega)$ for water at 293 K.

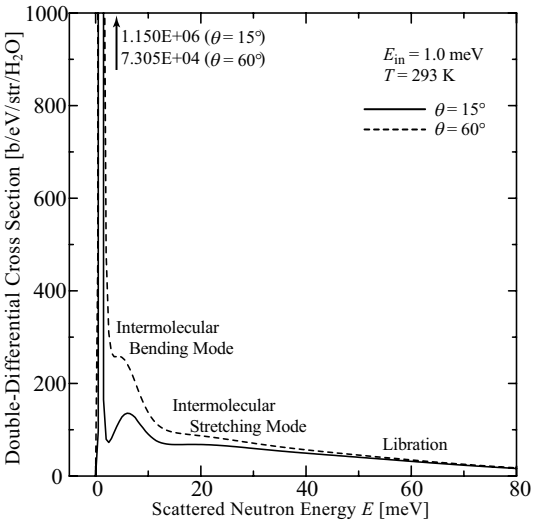

Fig. 2. Behavior of $\mathrm{d}^2\sigma_\mathrm{s}/\mathrm{d}\varepsilon\mathrm{d}Q$ for water at 293 K with E_0 = 1.0 meV and θ = 15° and 60°.

$F_\mathrm{s}(Q,t) = \exp[-Q^2W(t)/2]$ where Q is the momentum transfer as $Q\hbar$ and $W(t)$ is the width function as a mean squared displacement of molecule during t. By the numerical Fourier transform of $F_\mathrm{s}(Q,t)$ with respect of t ranging from ~0.001 to ~100 ps, various scattering cross sections can be determined: a scattering law

$$S_\mathrm{s}(Q,\omega) = \frac{1}{2\pi}\int F_\mathrm{s}(Q,t)\exp(-\mathrm{i}\omega t)\,\mathrm{d}t \tag{1}$$

$$= 2S_\mathrm{H,s}(Q,\omega) + \left(\frac{b^2_\mathrm{O,inc}+b^2_\mathrm{O,coh}}{b^2_\mathrm{H,inc}+b^2_\mathrm{H,coh}}\right)S_\mathrm{O,s}(Q,\omega), \tag{2}$$

a double-differential cross section

$$\frac{\mathrm{d}^2\sigma_\mathrm{s}}{\mathrm{d}\varepsilon\mathrm{d}Q} = \frac{1}{\hbar}\left(b^2_\mathrm{H,inc}+b^2_\mathrm{H,coh}\right)\frac{k}{k_0}S_\mathrm{s}(Q,\omega), \tag{3}$$

by the incoherent approximation, an angular distribution $f(\theta)$ and a total cross section $\sigma_\mathrm{t}(E_0)$ where $\varepsilon = \omega\hbar$ is the energy transfer and θ is the scattering angle, E_0 is the neutron incident energy, k_0 and k are the wavenumbers of incident and scattered neutrons, respectively.

3 Molecular Dynamics and Scattering Results

Fig. 1 shows $D(\omega)$ as a function of ε, together with the those by experiment [3] and molecular dynamics [4]. The one for H has a dominant component around 60 meV by the hindered rotation of molecule and a lower-energy component consisting of the translational diffusion near 0 meV and the translational stretching and bending vibrations around 6 and 20 meV. The one for O, however, indicates mainly the motions of center-of-mass in terms of translational stretching and bending vibrations. Intramolecular vibrations with the characteristic energies of 200 and 463 meV are beyond the energy range shown. It is also to be noted that $\phi(t)$ and $F_\mathrm{s}(Q,t)$ are found to be consistent with the recent molecular-dynamics results [5] at many different temperatures.

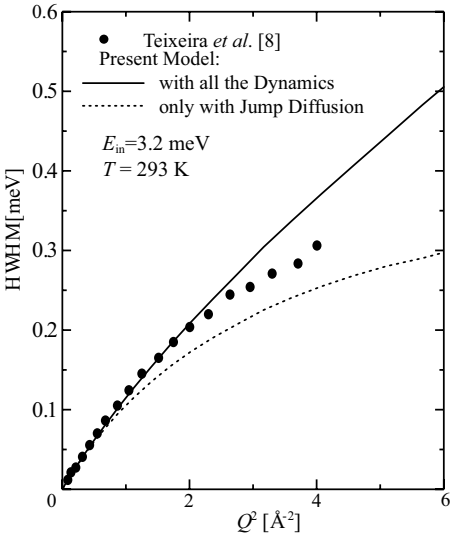

Fig. 3. The half-width at half maximum for the quasi-elastic scattering in water at 293 K with E_0 =3.2 meV.

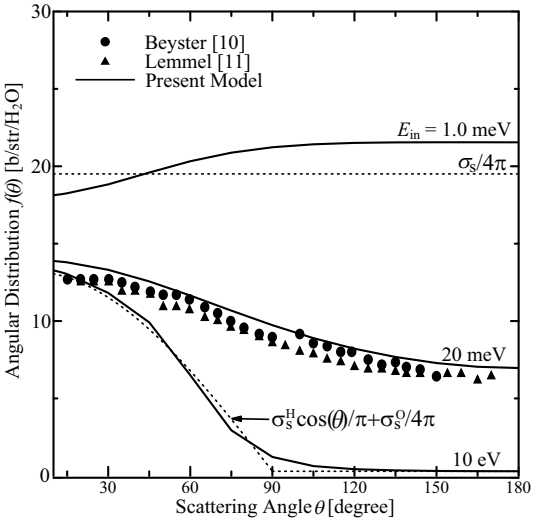

Fig. 4. Behavior of $f(\theta)$ for water at 293 K with E_0 = 1 meV, 20 meV and 10eV.

Fig. 2 shows $d^2\sigma_s/d\varepsilon dQ$ of light water at 293 K for θ = 15° and 60° with E_0 = 1 meV. They are composed of two components: a very high and sharp peak by quasi-elastic scattering due to the jump and rotational diffusion processes and a relatively broad peak by inelastic up-scattering arising from the de-excitation of intermolecular vibrations and hindered rotations. With an increase in θ, the quasi-elastic peak becomes broad and small to overlap the inelastic peak. Comparison with the experimental results [6, 7] for water at 299 K with E_0 = 5, 151 and 304 meV is satisfactorily made.

Fig. 3 shows the half-width at half-maximum for the quasi-elastic peak of water at 293 K as a function of Q^2. Also shown is the experimentally-estimated results for the quasi-elastic component extracted from the data [8]. The solid line includes all the dynamics modes while the broken line with only the jump diffusion process. Consequently, the latter is relatively similar in saturation behavior with the experiment. Such an analysis is performed successfully in comparison with those on neutron scattering at many different temperatures [6, 9].

Fig. 4 shows $f(\theta)$ for the three different E_0, compared with the experimental results [10, 11]. For a 10-eV neutron, forward scattering in a free H is significant. On the contrary, a 1-meV neutron scatters nearly isotropically though a backward up-scattering is slightly seen by the de-excitation of intermolecular vibrations and librations. The result of a thermal neutron indicates a mid-behavior between the above extremes.

4 Group Constant and Scattering Law

As a powerful tool for the design assessment of practical cold neutron sources, a set of group constants for liquid water is generated. Light water at 5, 27, 52 and 77 °C is evaluated by using the cross section model. The energy range from 0.1 μeV to 10 eV is divided at equal logarithmic (lethargy) intervals into 80 groups. The angular distribution of scattering cross section is represented by the Legendre expansion up to a maximum order 3 which is almost adequate for reproduction of forward scattering in free atoms, H and O, by an epithermal neutron. The weighting flux is a Maxwellian plus $1/E$ spectrum with the same temperature as water.

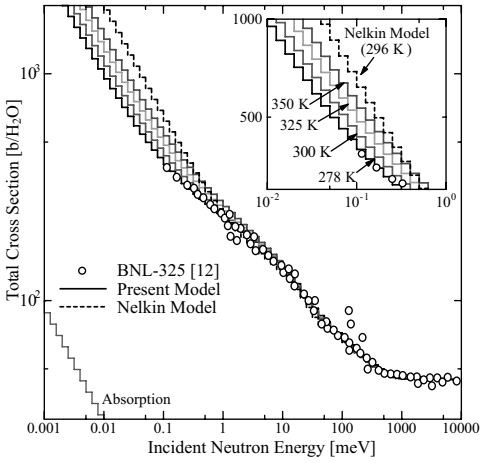

Fig. 5. Behavior of σ_t and σ_a for water at 278, 300, 325 and 350 K.

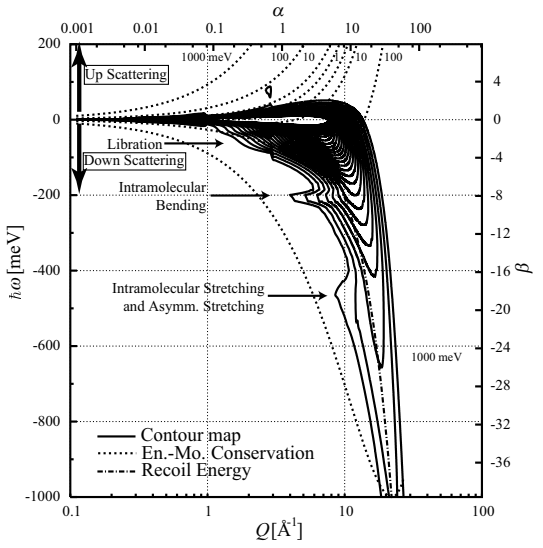

Fig. 6. Contour map of $S_{H,s}(Q,\omega)$ for water at 293 K.

Fig. 5 shows the group-constant results of σ_t and total absorption cross section σ_a for water at four different temperatures. Also shown are the experimental results from BNL-325 [12] and the ones by the Nelkin model at 296 K [13]. With an increase in T, up-scattering at lower energies below about 1 meV becomes significant, while σ_t approaches a free atom cross section of 44.6 b/H_2O at energies above about 1 eV. It can be seen from Fig. 5 that there are good agreement with the experiment at ordinary temperature and essential difference in σ_t between liquid water and molecular gas. It may be also noted that the calculated average cosine of θ indicates a gradual transition from forward scattering to uniform one with decreasing E, which agrees well with the experimental result [10].

Along with the group constant generation, a data file of $S_s(Q,\omega)$ is created in the ENDF/B-VI format. A wide range of momentum and energy transfer is covered: $Q = 0.11$ to 35 Å^{-1} and $\hbar\omega = -10$ eV (down scattering) to 100 meV (up scattering), which correspond to α ($= \hbar^2 Q^2/2mkT$) from 0.001 to 100 and β ($= \hbar\omega/kT$) from -400 to 4, respectively, where m is the neutron mass and $kT = 25.24$ meV at 293 K. Fig. 6 shows a typical result of $S_{H,s}(Q,\omega)$ for water at 293 K. At smaller Q, the intermolecular dynamics inherent to liquid water are significant while, at larger Q, the intramolecular motions and the recoil scattering in free H atom become effective.

5 Concluding Remarks

(a) The physical properties of hydrogen-bonded liquid water have still remained unsettled especially from a microscopic viewpoint. Hence a neutron scattering study is planned to determine directly $F_s(Q,t)$ by means of a neutron spin echo (NSE) technique [14]. Temperature dependences of intermolecular modes and diffusion processes will probably be observed both for light and heavy water. Among many variations of NSE spectrometers, the Mieze type would be most suitable for this experiment, since high experimental efficiency is attainable by very short distance between water sample and neutron detector: the NSE does not need an energy analyser after the sample and instead uses the Larmor precession as an internal measure of neutron energy. At present, such inelastic and quasi-elastic scattering is now being planned using a new Mieze spectrometer to be developed at the C3-1-2-2 beam port of the JRR-3M reactor.

(b) The present cross section model makes possible the systematic interpretation of neutron-scattering and molecular-dynamics results on $\phi(t)$, $D(\omega)$, $W(t)$, $G_s(r,t)$, $F_s(Q,t)$, $S_s(Q,\omega)$, $d^2\sigma_s/d\varepsilon dQ$, $f(\theta)$ and $\sigma_t(E_0)$. A wide range of usefulness is found for neutron energies from ultra-cold (0.1 μeV) to epithermal (10 eV) neutron areas and liquid temperatures between melting and boiling points. Furthermore, a set of group constants for light water at all practical temperatures is generated. Those for heavy water will soon be ready for use [15]. By the combined use of the already-generated group constants on liquid ^{4}He, H_2, D_2 and CH_4 and also solid CH_4 [16], we may proceed to the preliminary study of an advanced low-energy neutron source on ultra-cold, very cold and cold neutrons.

Acknowledgement

The authors sincerely thank Dr. Takamasa Mori of JAERI-Tokai for his valuable information on the thermal neutron scattering library.

References

[1] K. S. Singwi, A. Sjölander, *Phys. Rev.*, **119**, 863(1960).

[2] V. F. Sears, *Can. J. Phys.*, **44**, 1999(1966) .

[3] M. -C. Bellissent-Funel *et al.*, *Phys. Rev. E*, **51**, 4558(1995).

[4] G. C. Lie, E. Clementi, *Phys. Rev. A*, **33**, 2679(1986).

[5] D. Di. Cola *et al.*, *J. Chem. Phys.*, **104**, 4223(1996).

[6] M. Sakamoto *et al.*, *J. Phy. Soc. Japan, Sup. B-II*, **17**, 370(1962).

[7] O. K. Harling, *J. Chem. Phys.*, **50**, 5279(1969).

[8] J. Teixeira *et al.*, *Phys. Rev. A*, **31**, 1913(1985).

[9] F. Cavatorta *et al.*, *J. Phys.: Condensed Matter*, **6**, A113(1994).

[10] J. R. Beyster, *Nucl. Sci. Eng.*, **31**, 254(1968).

[11] H. D. Lemmel, *Nukleonik*, **7**, 265(1965).

[12] D. I. Garber, R. R. Kinsey, *BNL-325 Vol. II*, (1976).

[13] M. Nelkin, *Phys. Rev.*, **119**, 741(1960).

[14] S. Tasaki *et al.*, *Physica B*, **335**, 234(2003); S. Tasaki *et al.*, *Physica B*, **311**, 02(2002) .

[15] N. Morishima, Y. Aoki, *Ann. Nucl. Energy*, **22**, 147(1995).

[16] Y. Abe, N. Morishima, *Nucl. Instrum. Method A*, **481**, 414(2002); N. Morishima, Y. Matsuo, *Nucl. Instrum. Method A*, **490**, 308(2002); Y. Matsuo, N. Morishima, Y. Nagaya, *Nucl. Instrum. Method A*, **496**, 446(2003); Y. Sakurai, T. Mitsuyasu, N. Morishima, *Nucl. Instrum. Method A*, **506**, 199(2003).