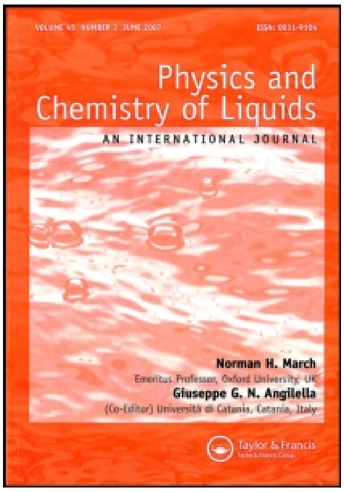

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# Structural Quantum Effects In Hydrogeneous Liquids And Glasses: Part I Review Of Early Methods And Experiments

P. A. Egelstaff[a]
[a] Department of Physics, College of Physical and Engineering Science, University of Guelph, Guelph, Ontario, Canada

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## *Review*

# STRUCTURAL QUANTUM EFFECTS IN HYDROGENEOUS LIQUIDS AND GLASSES: PART I REVIEW OF EARLY METHODS AND EXPERIMENTS

P.A. EGELSTAFF

*Department of Physics, College of Physical and Engineering Science,*
*University of Guelph, Guelph, Ontario, Canada*

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The atomic or molecular structure of simple liquids may be studied experimentally through radiation scattering experiments. Normally, these experiments involve either beams of E-M radiation or of thermal neutrons, and frequently the samples included both hydrogenated and deuterated liquids. In order to interpret such data it has been assumed (frequently) that the liquid structure was unchanged when the H/D composition was changed. Similar comments apply to hydrogeneous glasses.

As the quality of the data and of model calculations improved with passing years, limits to these assumptions were discovered. Part I of this review will cover both the background material and the research which led to an understanding of this field, and also determined the magnitude and shape of the observable effects. Subsequent research from the 90s onwards will be reviewed in Part II.

*Keywords:* Radiation scattering; Hydrogenated and deuterated liquids

## 1. INTRODUCTION

The study of molecular quantum effects in liquids at various temperatures came alive in the 80s with experiments and calculations on light and heavy water. There were separate X-ray experiments on low temperature amorphous ice [1,2], and carefully interrelated $\gamma$-ray experiments on room temperature water [3,4]. In parallel there were

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computer simulations on this topic for water [5a,b]. All these studies led to the conclusion that changing H to D in a simple molecule produced observable structural changes in the liquid or the amorphous ice. Thus the small differences in molecular or intermolecular dimensions and motions, between hydrogeneous and deuterated fluids and glasses, will lead to small changes in the intermolecular structure which are observable in carefully designed experiments. The possible applications of these ideas and results to other areas of science is a very interesting topic, but it is outside the scope of this review. However, the understanding of these effects then led to more detailed studies in the 90s and later, which involved a variety of samples and which will be discussed in Part II.

Here we begin by describing radiation scattering techniques and their application to this area of science. Then the growth and development of this field will be discussed via the early data (mainly from the 80s) which will be reviewed. The effects being studied here are relatively small, and therefore advanced experiments and careful theoretical calculations are required which together will move the frontier to this field forward.

The principles of radiation scattering experiments are the same for the various kinds of radiation that are employed, and Fig. 1 illustrates the standard geometry. An incident beam (of wave vector **k**) falls on the sample and the intensity of scattered radiation into the angle $\theta$ is

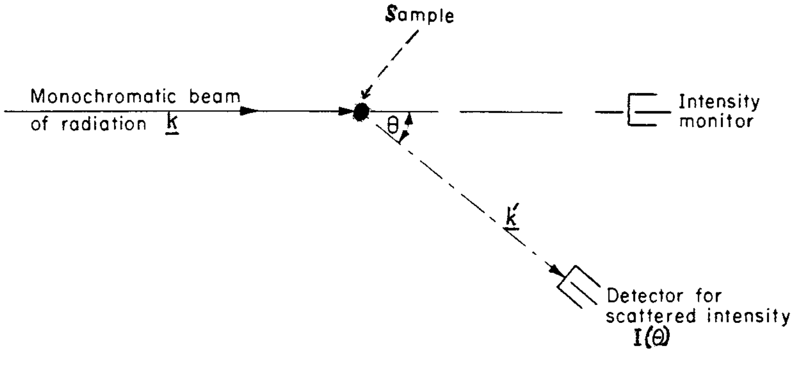


FIGURE 1 Schematic layout of a radiation scattering experiment; the shielding on the beam lines and the detector is not shown. The momentum transfer is $\mathbf{k} - \mathbf{k}' = \mathbf{Q}$, and is adjusted to the value for elastic scattering.

measured. If the energy transfers are small compared to the incident energy, then the variations in the scattered wave vector ($\mathbf{k}'$) are small and the data may be corrected to the equivalent of elastic scattering. The relevant parameter then becomes the momentum transfer $\hbar\mathbf{Q}$. Since the samples being discussed here are isotropic, only the magnitude of $\mathbf{Q}$ (denoted by $Q$) is relevant. Also there will be a spread in $Q$ values due to features of the instrument (e.g. the angular and energy resolution), and provided these are small, the data may be corrected to that for a mean value of $Q$.

Thus the experiment consists of measuring the scattered intensity from a thin sample as a function of $Q$. Then after several corrections are applied (e.g. for absorption and multiple scattering effects etc.), the data on corrected scattered intensity versus $Q$ may be placed on an absolute scale and presented as the structure factor $S(Q)$ versus $Q$. There are several choices of normalization for $S(Q)$, and here we shall relate $S(Q)$ for high $Q$ to the number of electrons per molecule. As an example of its interpretation, the quantity $S(Q)$ for liquid water is composed of the sum of three partial $S(Q)$s, one each arising from HH, OO, or OH atomic correlation functions. Finally, each of these partial $S(Q)$ functions Fourier transforms into a corresponding partial atomic correlation function. The E-M radiation diffraction experiments are sensitive mainly to the (OO) correlation function, while the neutron diffraction experiments see a mixture of all three functions but have a different weighting among the three correlation functions for light or heavy water specimens.

Therefore, normalized data from these radiation scattering experiments may be Fourier transformed into pair correlation functions [6]. They describe the probability distribution of finding atom A at any given distance ($r$) from atom B, and (as stated above) if the sample is composed of two kinds of atoms (for example) there will be three different functions of this kind. In the next section, the methods of separating and studying these functions using E.M. radiation and thermal neutron scattering will be discussed. However, for many neutron experiments on hydrogeneous samples, this will involve the (poor) assumption that H and D liquid isotopic samples have the same structure in order to separate the data into the several partial structure factors. As stated above, the limitations of this assumption were first revealed clearly in reference [3,4,5a].

## 2. DISCUSSION OF RADIATION SCATTERING EXPERIMENTS

A review of the methods used to conduct and interpret radiation scattering experiments on fluids has been given by Egelstaff [7] and a summary of the equations used to interpret the data is given in an appendix. We begin by comparing three kinds of radiation which may be used in these experiments as shown in Table IA. They are E-M radiation, electrons or neutrons. E-M radiation is scattered mainly by the electrons rather than the nuclei because there is a 1/mass factor appearing in the cross section. Two cases are listed, where either one interprets the scattering as coming from each atom as a whole, or from each electron: however, normally the first case is used since the usual objective will be to convert the data into an atomic or molecular distribution rather than an electronic distribution. The third case in this table is that of electron scattering, but since the penetration of matter by electrons (with a wavelength $\sim 1$ Å) is small, they are of limited use for this field. Finally, for neutron scattering the targets are the atomic nuclei and therefore the nuclear correlation functions are observed directly. Because the neutron scattering amplitudes for hydrogen and deuterium are different, it is possible (in principle by conducting a series of scattering experiments on samples of differing isotopic composition) to separate out the distribution functions for the several pairs of atoms e.g. (O,O), (O,H) and (H,H) in the case of water. But for this step to be successful, it is necessary to assume that the inter-molecular structures of light and heavy water are exactly the same. Later we shall discuss the limits to this assumption, and describe experiments which allow quantitative corrections to it to be determined. A comparison between these various kinds of radiation is given in Table IB.

Because neutrons and X-rays are the most useful and most commonly used radiations for experiments in this field, it is useful to compare their properties. This is done in Table II. Slow neutrons have useful properties for many experiments, but unfortunately the scattering from hydrogen is dominated by incoherent scattering which is not sensitive to liquid structure. This makes it difficult to exploit isotope difference effects on samples like water, and often experiments are conducted with deuterium isotopic samples only.

TABLE IA Properties of three kinds of radiation ([7], p.8)

| *Radiation* | *Scattering center* | *Scattering centre size (relative to size of atom)* |
|---|---|---|
| Electromagnetic | Atomic electron density | 1 |
| Electromagnetic | Each electron | 0 |
| Electrons | Atomic charge density | 1 for electronic charge<br>0 for nucleus |
| Neutrons | Each nucleus | 0 |

TABLE IB A comparison of several kinds of radiation

| *Radiation* | *Wavelength* Å | *Target* | *Use* | *Notes* |
|---|---|---|---|---|
| Fast neutrons | ~0.05 | Nuclei | None | Theoretically the best |
| $\gamma$-rays or synchrotron rad. | ~0.05 | Electrons | None (Liquids) | Theoretically the best |
| Electrons | ~0.05 | Nuclei and electrons | Some | Useful but difficult |
| Slow neutrons | ~1 | Nuclei | Wide | Needs more corrections than fast neutrons |
| X-rays | ~1 | Electrons | Wide | Needs more corrections than $\gamma$-rays |

TABLE II Properties of neutrons and X-rays

| *Ideal Property* | *Neutrons* | *Traditional X-rays* |
|---|---|---|
| Penetrates matter easily | Yes | No for heavy atoms |
| Reasonable size samples | Yes (in many cases) | Yes |
| Long life time | Yes | Yes |
| Competing cross sections | No | Yes |
| Sees atoms centre of mass | Yes | No |
| Sees isotopes differently | Yes | No |
| Sees electron distribution | No | Yes |
| Sees magnetic moments on atoms | Yes | No[a] |
| Energy transfers seen | Yes | No[a] |
| Right wavelength | Yes | Yes |
| Widely available | No | Yes |

[a] These effects occur and may be observed in some synchrotron radiation experiments.

Neutrons also have the advantages for some experiments of having measurable energy exchanges with the sample, and (in general) of the data being unaffected by competing scattering processes. In contrast, the energy changes on scattering are not observed (conventionally) with X-rays, and also Compton scattering is an additional process which must be calculated or measured and subtracted from the total scattered intensity.

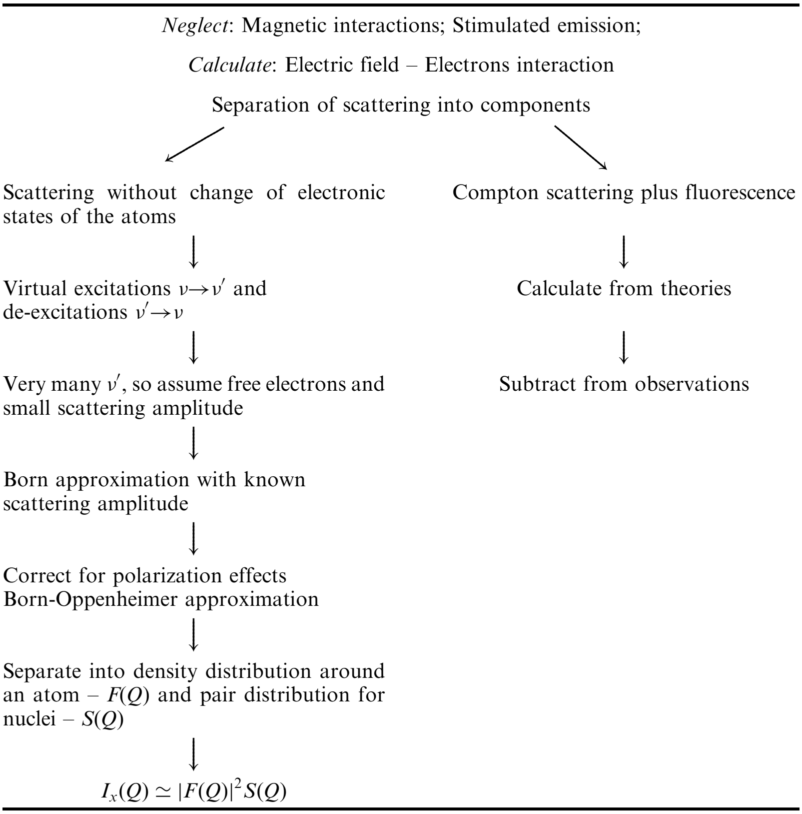
Since neutrons are scattered by the atomic nuclei, the nuclear correlation functions are measured directly. However, for X-rays they are deduced from the scattering by the atomic electrons, and a knowledge of the electronic form factors for each atom or molecule. Unfortunately, since neutrons are not universally available, they are used much less frequently than X-rays. But for the present objective of determining the differences in the structures between hydrogeneous and deuterated liquids, X-rays (or other E-M radiation) are the obvious choice. For such measurements, the source should be intense and the wavelength should be small, so that accurate comparisons may be made, since the experimental corrections are then minimized. Once the difference between the H and D isotopic liquids or glasses has been measured, it should be possible to reinterpret the neutron scattering data for the same samples in order to derive more accurate partial structure factors.

## 3. DISCUSSION OF THE STEPS IN DATA REDUCTION TO $S(Q)$

It is useful to understand the limitations to radiation scattering experiments caused by the theoretical steps involved in moving from the experimental data to the desired correlation functions. For electromagnetic radiation these steps are shown in the Appendix and in Table III, and the correction for Compton scattering is usually the largest. However, the theoretical expressions [8] are satisfactory. The specific application of Table III to X-rays and some comments on the practical aspects of X-ray techniques are given in Table IV. For the present applications of these methods it is important to note that the corrections to the data may be minimized by working with low angles of scatter. To do this over the normal ranges of momentum transfer requires the use of high energy incident radiation: for example 60 keV $\gamma$-rays or 100 keV synchrotron radiation. Experiments using these energies will be discussed later.

A similar listing of the steps in reducing the neutron scattering data to the Fourier transform $S(Q)$ of the pair correlation function are given in Table V. In many cases, the major experimental limitation arises at the last step, since the integration must be performed at constant $Q$.

TABLE III Scattering of electromagnetic radiation by matter ([7])



*Neglect*: Magnetic interactions; Stimulated emission;

*Calculate*: Electric field – Electrons interaction

Separation of scattering into components

Scattering without change of electronic states of the atoms

Virtual excitations $\nu \rightarrow \nu'$ and de-excitations $\nu' \rightarrow \nu$

Very many $\nu'$, so assume free electrons and small scattering amplitude

Born approximation with known scattering amplitude

Correct for polarization effects
Born-Oppenheimer approximation

Separate into density distribution around an atom – $F(Q)$ and pair distribution for nuclei – $S(Q)$

$I_x(Q) \simeq |F(Q)|^2 S(Q)$

Compton scattering plus fluorescence

Calculate from theories

Subtract from observations

However, the collection of data at each angle involves an integration over all energy transfers between the incident neutrons and the sample. This process means that each experimental point covers a range of $Q$, which may be reduced to a single $Q$ by a theoretical correction known as a Placzek [9] correction. Again this correction may be minimized by using higher incident energies, but usually this means lower neutron fluxes.

A comparison of these corrections for X-rays and neutrons is given in Table VI. The principal items are listed above the dashed line, while two other smaller effects are listed below it. Since the principal topic of this paper is structural quantum effects in hydrogeneous liquids, we need to summarize how these effects enter these two kinds of scat-

TABLE IV X-ray scattering by matter

*Some underlying points*

- X-rays see electrons and are easily absorbed;
- the theory given in Table III is good to $\sim 1\%$ only;
- only part of the scattering is useful with the standard analysis (Table III);
- the scattering amplitude varies with the angle ($\theta$);
- no method for the separation of individual elements in chemical compounds is available (conventionally); total atomic pair correlation function is a usual end-point;
- the dynamic distribution functions cannot be studied (conventionally);
- an alternative treatment with electrons as primary scattering centers is possible, but not used normally;
- X-rays can observe special effects e.g.:
  - bonding electron distributions
  - quantum effects in hydrogeneous fluids
- X-ray sources are many, and are relatively strong;
- many corrections may be reduced by using high incident energy radiation at low angles of scatter with thin samples.

TABLE V Neutron scattering by matter ([7])

*Neglect*: Neutron–Electron and magnetic interactions
*Measure*: Neutron–Nucleus scattering

↓

Partial wave analysis of nuclear scattering

↓

Neutron wavelength $\gg$ Nuclear size therefore $s$-wave terms only

↓

Fermi $\delta(r)$ nuclear potential and small scattering amplitudes

↓

Born approximation (weak scattering) with unknown scattering amplitude

↓

Integrate the scattering function $S(Q,\omega)$

↓

$$\int S(Q,\omega)d\omega = S(Q)$$

tering experiments. For neutron scattering we use samples containing either hydrogen or deuterium at specific locations in the molecules. If it is assumed that the change from H to D produces no structural changes (neither inter or intra-molecular), then the observed differences in the scattering data caused by this substitution are of great interest. This is because by writing the total scattering as a sum of partial scattering functions (one for each pair of inter-molecular

TABLE VI Comparison of corrections in typical cases (major corrections are those above the dashed line)

| *Type* | *X-rays* | *Neutrons* |
|---|---|---|
| Absorption | Large[a] | Not so large[a] |
| Multiple Scatt. | Not so large[a] | Large[a] |
| Inelasticity | Nil | Large (light atoms)[a]<br>Small (heavy atoms) |
| Polarizability | Large[a] | Nil |
| Fluorescence | Some[a] | Nil |
| Compton | Large | Nil |
| Form Factor | Large | Nil |
| Normalization | Various ways | Vanadium |
| --------- | --------- | --------- |
| Born approx. | Good | Very good |
| Other scattering | Magnetic | Electrons |

[a] Correction may be reduced or simplified by using high energy radiation at low angles.

sites), one obtains a set of data which allow each partial function to be extracted. For example, in the case of water there would be the O–H, the H–H and the O–H partial correlation functions, and we would need three measured scattering functions with different H/D ratios to determine all three partial correlation functions.

The underlying assumption here is that these partial correlation functions are unchanged by isotopic substitution. At high temperatures this may be a good assumption, but at room temperature or below, it will be necessary to evaluate corrections in detail. For example, Kuharski and Rossky [5a] have shown that these corrections are significant for room temperature water. In order to measure such effects, we have to turn to electromagnetic radiation scattering by the electrons in each molecule. To a first approximation the electrons follow the nuclei, and so E-M scattering will allow us to measure the structural differences caused by isotopic substitution. Also because these effects are small, it is necessary to use high energy incident radiation in order to minimize the corrections listed in Table VI.

In the remainder of this paper, the early development of this field using X-ray and $\gamma$-ray sources will be described, and the comparison of the results with computer simulations will be given. This comparison highlights both the significance and usefulness of these data. More recent work using powerful synchrotron sources and 100 keV radiation will be described in Part II.

## 4. EARLY RESULTS ON LIGHT AND HEAVY WATER

Water has been studied perhaps more than other liquids or amorphous materials. Here we shall describe experiments and calculations carried out in the 70s and 80s, and discuss later work in Part II.

(a) Amorphous Water: Light water samples made by vapor deposition at 10 K and 77 K were measured by Narten *et al.* [1] using conventional X-ray techniques. An example of these data – namely that deposited and measured at 77 K – is shown in Fig. 2a. Later heavy water samples were prepared, through the compression of crystalline ice 1 h to 2 GPa at 77 K, by Bizid *et al.* [2]. These samples had the structure of high density amorphous (HDA) ice, Whalley [10], and were converted to low density amorphous ice (LDA) by thermal processing at about 130 K. After cooling the LDA to 77 K X-ray diffraction measurements were made.

Bizid *et al.* [2] compared their data to that of Narten *et al.* [1] (shown in Fig. 2a) which was prepared and measured at 77 K. The difference between these two sets of data is shown in Fig. 2b, and the similarity of these two amorphous ices is clear. By comparing Figs. 2a and b it may be seen that peak magnitudes of the difference function average to about an order of magnitude lower than those in $S(Q)$. Bizid *et al.* [2] comment that the light water peaks are shifted slightly to the right of the heavy water ones, and that this is mainly due to the difference in O–O distances of 2.76 Å for light and 2.80 Å for heavy water. By comparing peak positions in Figs. 2a and b this effect may be examined. However, in this case the experiments were done on different instruments with samples prepared in different ways, and therefore the agreements may be within the possible uncertainties.

(b) Liquid Water: In order to make more exact comparisons, it is necessary to employ the same instrument and sample set-ups for both water specimens. Also it is worthwhile using high energy (i.e. short wavelength) radiation which leads to lower angles for scatter and thus smaller corrections. Root *et al.* [11] used a $^{241}$Am radioactive $\gamma$-ray source to obtain a beam of wavelength 0.208 Å radiation. In addition, such a source is very stable over time, both in wavelength, intensity and polarization. They studied light and heavy water at 297 K, and observed a difference in their structure factors. The difference in intermolecular correlation functions (light minus heavy) is shown in

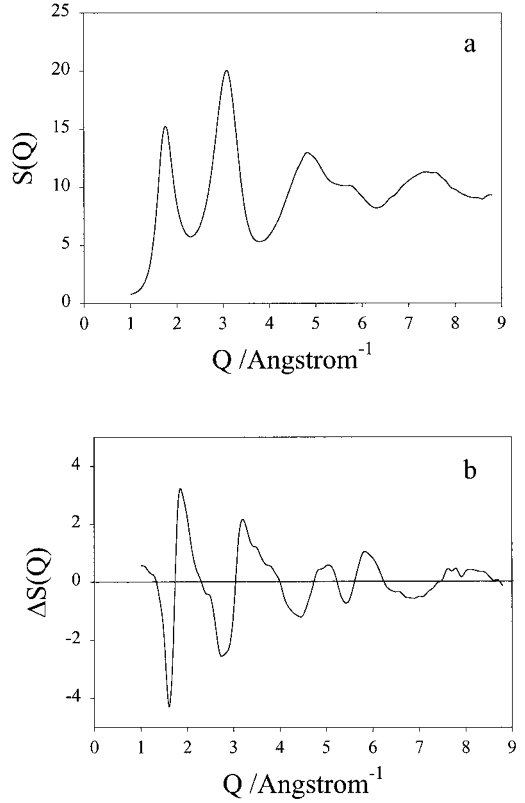


FIGURE 2 A comparison of the X-ray structure factors of low density amorphous ice at 77 K, for light water (1) and heavy water (2) specimens. This diagram is a modified version of Fig. 4 of Bizid *et al.* [2]. The smooth lines are drawn through the published data; (a) is the data of Narten *et al.* [1] and (b) is the $H_2O$–$D_2O$ difference.

Fig. 3. The data in *Q*-space is shown in Fig. 3a, while their Fourier transform to *r*-space is shown in Fig. 3b. In Fig. 3b the data are compared to the computer stimulations of Kuharski and Rossky [5a], and those of Del Buono *et al.* [5b]. Agreement to order of magnitude and in the general shape is found. In view of the pioneering nature of both these experiments and stimulations, this limited level of agreement was satisfactory. Figure 3c shows the room temperature *S*(*Q*) for water [12], and by comparison of Figs. 3a and c it may be seen that the first (low *Q*) peak in Fig. 3a has the same location as that in Fig. 3c, while the higher *Q* peaks in 3a correspond to valleys in 3c. It is also clear

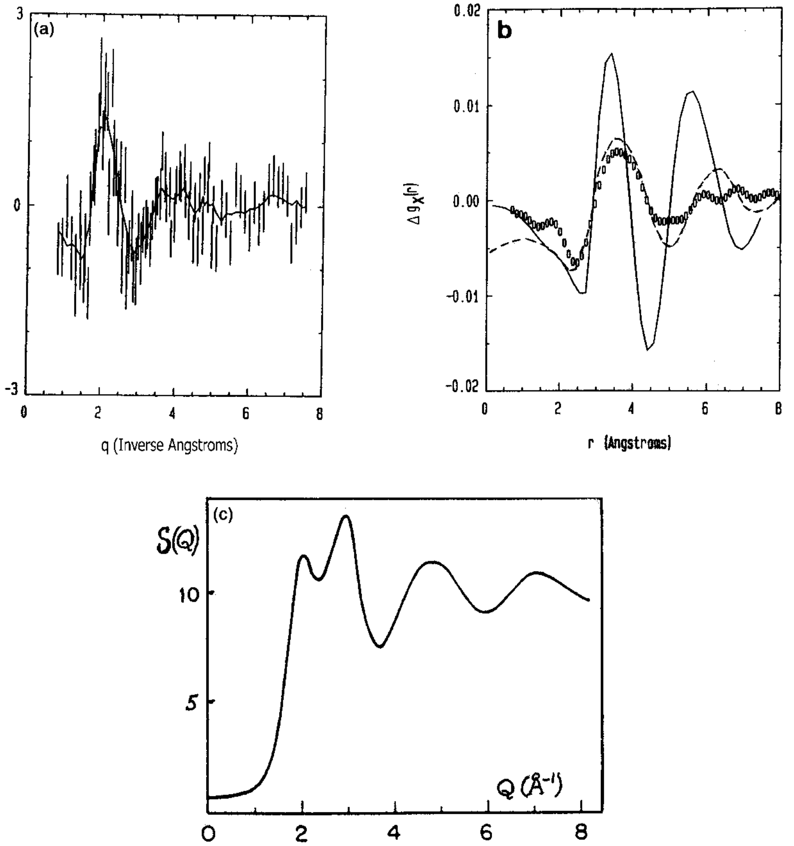


FIGURE 3 (a) The difference between the intermolecular correlation functions (in *Q* space, denoted by *D*(*Q*) of heavy and light water at 23 ± 0.5°C. The solid line is obtained by a maximum entropy smoothing procedure; (b) The Fourier transform of the data in (a) to *r*-space is shown by the circles, and the solid line is the computer simulation of Δg(*r*) by Kuharski and Rossky [5a] using the ST2 potential, and the dashed line is a later simulation by Del Buono *et al.* [5b] using the SPC potential; (c) The structure factor *S*(*Q*) for light water at 25°C from Narten *et al.* [12], a smooth line is drawn through the data. The positions of the peaks are compared to those in (a) in Section 4b.

that the effect of greater thermal broadening in the case of light water is significant in Fig. 3, in contrast to the structural effect in Fig. 2. Root *et al.* [11] point out that the simplest way to compare light and heavy water is to note that the structures are roughly the same when the heavy water is 5°C warmer than the light water.

## 5. STRUCTURAL QUANTUM EFFECTS IN LIQUID AMMONIA AND METHANOL

The example of water is one in which hydrogen bonding is important. Consequently, it would be interesting first to compare a non-H bonded example with that of water, and secondly to compare two different hydrogen bonded systems. For the first case, Takeda and Egelstaff [13] measured this effect in ammonia and for the second case Benmore and Egelstaff [14] measured this effect in methanol. In both cases the $^{241}$Am $\gamma$-ray diffractometer was used and procedures similar to those used for water were employed.

Figure 4a shows the experimental results [13] for liquid ammonia at 21.5°C, and it was found that shape and magnitude was similar again to a 5° shift in temperature. Surprisingly, the shape and magnitude of this curve is similar also to that shown for liquid water in Fig. 3b. However, a comparison of the data in Fig. 4a with the structure factor for ammonia [15] shown in Fig. 4b, shows that the maxima and minima in Fig. 4a correspond to minima and maxima, respectively, in 4b. This corresponds to sharper peaks for the deuterated liquid. Also this effect is stronger than that found for water, and probably reflects the simpler intermolecular bonding for ammonia.

Finally, the example of methanol [14] is shown in Fig. 5, where again effects of a similar magnitude were found. The lower arrows mark the positions of peaks in the methanol structure factor [16]. For $Q < 4\,\text{Å}^{-1}$ the observed effect is mainly intermolecular, while for larger $Q$ values it is close to the intramolecular calculation. By comparing these data with those for water (Fig. 3a), it may be seen that the shape is similar. To illustrate this, the positions of the peaks in Fig. 3a have been marked by arrows at the top of Fig. 5. The fact that this correspondence occurs may suggest that this sample had some water impurity, and this possibility will be discussed in Part II.

## 6. CONCLUSIONS

During the past 20 years, many improvements have taken place in the neutron and E-M radiation diffraction experiments on fluids.

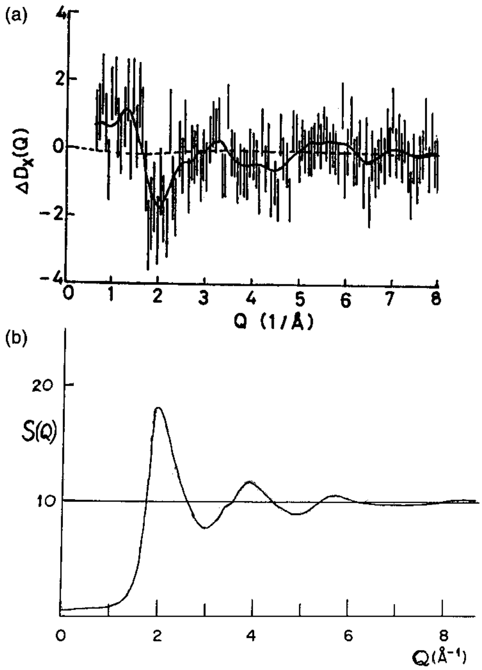


FIGURE 4 (a) The experimental difference $\Delta D_x(Q)$, between intermolecular scattering terms, $D_x(Q)$, for liquid hydrogeneous and deuterated ammonia at 21.5°C. The vertical lines are the error bars and the full line is the most probable line through them. For comparison, the dashed line shows the calculated isotopic difference between single molecules; (b) The liquid structure factor for hydrogeneous ammonia [15]: a smooth line is drawn through the experimental data.

High precision experiments are now possible using samples made of separated isotopes. In order to interpret such detailed and accurate results, it is necessary to employ sophisticated methods for comparing different isotopic samples. Here we have described how this may be done (for hydrogeneous samples) by using both E-M radiation data and neutron scattering data in an overall analysis.

It is particularly important that the inherent corrections in both techniques be reduced to a minimum, while retaining high statistical accuracy. With modern neutron and E-M sources this refinement is possible. However, it requires also a wide understanding of the underlying features of each technique, and by a series of tables (1 through 6)

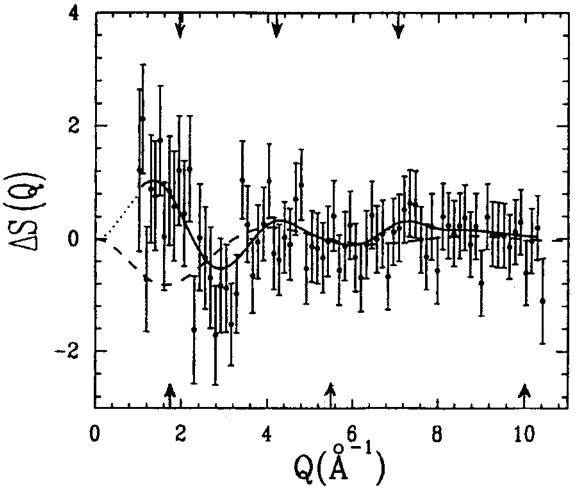


FIGURE 5 The experimental difference $\Delta S(Q)$ between hydrogeneous and deuterated methanol at 23°C is shown by the points and error bars. A maximum entropy smoothed fit is shown by the full line, and the contribution of the molecular form factor is given by the dashed line. The lower arrows mark the positions of peaks in the methanol structure factor [16], and the upper arrows mark the positions of peaks in Fig. 3a.

summarizing and comparing several features it is possible that a more detailed understanding of the field will be achieved? Then, as this field develops, it is hoped that this detailed understanding will prove to be beneficial.

The initial phases of our program have consisted of scattering experiments using high energy E-M radiation, and they had the object of measuring the differences between hydrogeneous isotopic samples, which in the past had been assumed frequently to be identical.

Initial experiments using an $Am^{241}$ radioactive source demonstrated that this objective could be met, and also indicated that many interesting scientific issues arose from comparing various sets of these data. Thus the next phase should be to extend and improve these experiments by using modern synchrotron sources of 100 keV radiation, and the first such experiments (on room temperature water) have been published [17]. The aim was to obtain high precision data for the structure factors and ensure that the comparisons and their interpretations are meaningful. These developments and further experiments will be described in part II.

## ACKNOWLEDGEMENTS

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## APPENDIX

### Equations Used to Interpret X-ray and Neutron Scattering from Molecular Liquids

The structure factor $S(Q)$ may be broken into an intramolecular $\langle F^2\rangle$ and an intermolecular part $D(Q)$ as follows:

$$S(Q) = \langle F^2\rangle + D(Q) \tag{A1}$$

In the case of E.M. radiation, the observed intensity $I(Q)$ must be corrected for the Compton scattering, $C(Q)$, in order to obtain $S(Q)$ (using literature values for $C(Q)$):

$$S(Q) = I(Q) - C(Q) \tag{A2}$$

However, for neutron scattering $S(Q)$ is obtained directly.

The intramolecular term is usually calculated for an isolated molecule. For E.M. radiation it is:

$$\langle F^2 \rangle = \sum_i \sum_j f_i f_j \frac{\sin_{ij} Q}{r_{ij} Q} \exp(b_{ij} Q^2) \tag{A3}$$

Here the sum is over all scattering centers $(i,j)$ in the molecule having spacial separation $r_{ij}$ and positional variances $b_{ij}$. For neutron scattering the quantities $f_i$, $f_j$, are constants, while for E.M. radiation the $Q$-dependent free atom form factors are used generally.

The three functions in Eq. (A1), appear in several formulae and in the figures. However, the units for $S(Q)$ vary among papers in the literature. Here the scale used is the number of electrons per molecule. An alternative would have been to normalize it to the nuclear composition of the molecule.