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The local bonding in water from -20 to 220°C

K Szornel†||, P A Egelstaff†, G E McLaurin‡ and E Whalley§

† Physics Department, University of Guelph, Ontario, Canada

‡ Steacie Institute for Molecular Sciences, National Research Council, Ottawa, Canada

§ Chemistry Division, National Research Council, Ottawa, Canada

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Abstract. It is believed that the mean distance between water molecules increases with a decrease in water temperature below room temperature due to the increase in 'hydrogen bonds', which implies an increase in the local fourfold coordination. In order to investigate how far this effect extends over a wider range, we have made constant-density measurements of the principal peak of the neutron structure factor of heavy water as a function of temperature. Data were taken at densities from 10% greater to 8% less than the maximum density at 1 atm, and for temperatures extending from -20 to 220°C . The effects seen at ambient conditions were found to extend over this whole range.

1. Introduction

The density maximum seen as a function of temperature in water at 1 atm pressure is usually associated with the phenomenon of hydrogen bonding and the related development of fourfold coordination. It has been argued that this form of packing requires greater volume than for a random packing of molecules, and that the fraction of molecules involved in this way increases with decreasing temperature. Consequently, at 1 atm pressure the mean distance between neighbouring molecules will increase with decreasing temperature, and eventually offset the usual contraction effects, so leading to the density maximum.

One theoretical method for studying the behaviour of hydrogen bonding as a function of pressure and density involves making molecular-dynamics simulations of water using a model intermolecular potential. This has been done by Mountain (1989), for example, who studied densities from 100 to 1000 kg m^{-3} and temperatures from 273 to 1130 K . He showed that the hydrogen-bond peak in the OH pair correlation function persisted over a wide range of temperature and density. Thus an experimental study of structure covering many states over a range of variables seems desirable, but unfortunately such an extensive study would necessitate that each measurement should be uncomplicated and of short duration.

The behaviour of the mean distance between neighbouring molecules may be observed through diffraction measurements. For example the liquid structure factor, $S(Q)$, observed in neutron-diffraction experiments on heavy water, (e.g. Gibson and Dore 1983) has a principal maximum near $Q = 20\text{ nm}^{-1}$. Frequently the data are plotted in a summary form: thus the position of the maximum (Q_0) has been plotted (e.g. Bosio *et al* 1983) as a function of temperature at 1 atm for temperatures between -15 and $+80^\circ\text{C}$. As discussed in section 2 a reduction in Q_0 with decreasing temperature usually indicates an increase in the mean separation of neighbouring molecules. Thus the effect described in the first

|| Present address: AECL Research, Chalk River, Ontario, Canada.

paragraph may be observed in Q_0 experiments over a wider range than is possible through measurements of a property such as density alone.

Two possible limitations to current work on the behaviour of Q_0 have been suggested. The first is that the temperature variation at 1 atm leads to variations in density as well as temperature, which may complicate the interpretation. Thus, this experimental method would be more convincing if it employed a constant density with some variation of temperature. Because this requires high-pressure work involving temperatures between -20 and 200°C , it is a difficult experimental task. In this paper we shall describe how we overcame these difficulties, and were able to study this effect along several isochores.

The second question is whether $S(Q)$ is the most appropriate function to use. This is related to the fact that the total structure factor may be written as the sum of three partial structure factors, which correspond separately to O–O, O–D, and D–D correlations. The experimentally observed function is a weighted sum of them, (see, e.g., Soper and Phillips (1986) who worked at room temperature and 1 atm). For a molecular liquid Q_0 is defined as the most probable Fourier component of the orientationally averaged molecular pair correlation function (see, e.g., Gubbins *et al* 1973), and therefore $2\pi/Q_0$ is similar to, but not the same as, the mean distance between molecular ‘centres’. A molecular centre may be defined in several ways, e.g. centre of mass, scattering centre, oxygen atom, etc. For our case, we use the scattering centre, which is the molecular centre using each atom’s scattering amplitude as its weight. Because of this definition, when the experimental conditions are satisfactory Q_0 should be also the position of the lowest peak in each of the partial structure factors. In figure 1 we show calculations (Lie *et al* 1976) of the partial structure factors for water to illustrate the coincidence of first-peak positions; this condition may be verified by figure 6 of Soper and Phillips (1986).

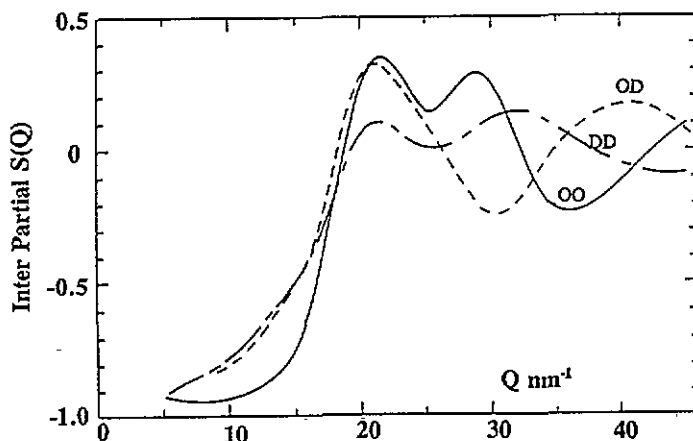


Figure 1. Calculated intermolecular partial structure factors (Lie *et al* 1976) for water at room temperature. The intramolecular contribution $S_{\text{intra}}(Q)$ is a smoothly falling background over the range illustrated here. When the three intermolecular components are combined with proper neutron weighting factors to form the observable $S(Q)$ —see equation (1)—it is found that the OD function contributes 75% of the peak at 20 nm^{-1} .

For the case of heavy water the observed $S(Q)$ is composed of fractions as follows:

$$S(Q) = S_{\text{intra}}(Q) + 0.486S_{\text{DD}}(Q) + 0.422S_{\text{OD}}(Q) + 0.092S_{\text{OO}}(Q) \quad (1)$$

where S_{intra} denotes the intramolecular term and the subscripts O and D denote oxygen and deuterium functions respectively. It should be noted that because the difference $S(Q) - S_{\text{intra}}(Q)$ can be negative, the partial structure factors may exhibit negative regions (see, e.g., figure 1). After multiplying the functions in figure 1 with the scale factors in equation (1) it may be seen that the largest contributor to the peak in $S(Q)$ near 20 nm^{-1} is $S_{\text{OD}}(Q)$. However we shall use only the total sum given in equation (1).

The conventional way to separate the data into these three terms is to make neutron-scattering measurements on several different mixtures of heavy and light water, and to assume in the interpretation that the structure is independent of molecular type. The latter approximation involves neglecting the different quantum effects associated with these two kinds of molecule. However, these quantum effects contribute strongly to the differences in the temperatures of the melting points and density maxima and, therefore, to the behaviour we wish to study. Consequently, the conventional separation method into partial structure factors requires extensive theoretical corrections for isotopic differences if accurate functions are to be achieved. The magnitude of such differences has been measured by Root *et al* (1986) using electromagnetic radiation and their results agree with theory (near Q_0 this effect is about 2%). Usually these differences are ignored by the experimentalists using neutron diffraction because the sum of their experimental errors is greater than the size of the quantum effects. Thus the partial-structure-factor method is unsuitable for a survey both because of its large errors and because of its very long measurement times. Measurements taken only in the neighbourhood of Q_0 may be interpreted straightforwardly as discussed also in section 2, and they have the experimental advantage of allowing a survey to be made over a wide range of states (see, e.g., table 1) because they can be made accurately in a short time.

We have built an apparatus that allows isochoric measurements of heavy water over -20 – 220°C to be made on a standard neutron diffractometer. This apparatus and the neutron-scattering measurements are described in section 3. The paper is concluded with a summary of the results and their discussion. In particular, we shall test some general ideas that might follow from interpretations of earlier experiments and also test the temperature scaling proposed by Egelstaff and Polo (1986) in their study of the thermodynamic derivatives of $S(Q)$.

2. Background

The aim of this section is to provide some background information on the calculated variation of Q_0 with temperature at constant density for a number of model cases. The simplest example is that of the uniform fluid (see, e.g., Egelstaff *et al* 1971) in which all distances vary as $(\text{density})^{-1/3}$ irrespective of temperature. Examples of this kind are the hard-sphere fluid and the ideal liquid metal (see, e.g., Ziman 1964). In the latter case it is necessary that the Fermi temperature of the electron gas is much greater than the specimen's temperature, and for example Egelstaff *et al* (1980) have shown that this model gives a good fit to the temperature and density variations observed in liquid rubidium. For the uniform-fluid model Q_0 does not vary with temperature at constant density.

Another case is that of noble gases or the Lennard-Jones fluid, for which the uniform fluid model fails (see, e.g., Egelstaff *et al* 1971). Here an effective-diameter model (see, e.g., Barker and Henderson 1967) may be used, and in this model the effective diameter decreases slightly with increasing temperature. This leads to Q_0 increasing slightly with

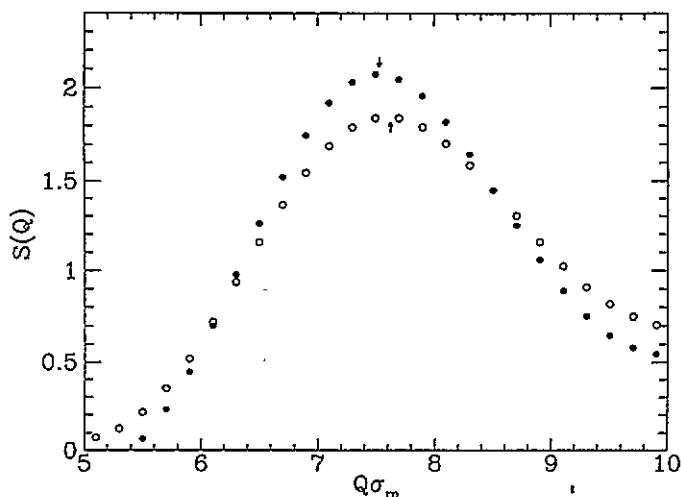


Figure 2. A computer simulation of the structure factor for krypton using the Aziz potential truncated at $3.56\sigma_m$ (Denton 1994). Solid circles correspond to 140 K and open circles to 300 K, for a density in non-dimensional units $\eta = \frac{1}{6}\pi\rho\sigma_m^3 = 0.59$ where σ_m is the position of the minimum in the pair potential and ρ is the number density. The arrows mark the positions of Q_0 .

temperature, and this effect may be observed readily in computer simulations, as shown for example in figure 2 (Denton 1994).

The opposite behaviour may be found in some models of molecular fluids. If an anisotropic potential (for example a dipole or quadrupole term) is added as a perturbation to the isotropic potential of the previous example, it may be shown (see, e.g., Wang *et al* 1973), that the major peak in $g(r)$ moves to lower r and the major peak in $S(Q)$ moves to higher (Q) . Therefore, for models of molecular fluids, where the anisotropic perturbation is largest at low temperatures and decreases slowly with increasing temperature (possibly enlarged through a temperature-dependent anisotropic term), the value of Q_0 will decrease slightly with temperature.

From these examples it may be seen that a variety of behaviours are possible. The way Q_0 varies depends mainly upon the variation of nearest-neighbour distances, and to preserve constant overall density the fluid will make some compensating changes at greater distances, which have a lesser effect on Q_0 . Therefore the magnitude of the variation of Q_0 with temperature at constant density depends sensitively on the nature and behaviour of the intermolecular forces.

The models discussed above are essentially atomic models, but the meaning attached to the location of the major peak in $S(Q)$ may be extended to simple molecular liquids. For our study it is convenient to write $S(Q)$ as (see Gubbins *et al* 1973)

$$S(Q) - S_{\text{intra}}(Q) = \rho \int_V e^{iQ \cdot R_{12}} \{g(R_{12}, \omega_1 \omega_2) - 1\} F(Q, \omega_1) F^*(Q, \omega_2) \}_{\omega_1 \omega_2} dR_{12} \quad (2)$$

where ρ is the molecular number density, ω_i is an angular variable and the angular dependent scattering amplitudes are

$$F(Q, \omega_i) \equiv \left(1 / \sum_{\alpha} b_{\alpha}\right) \sum_{\alpha} b_{\alpha} e^{iQ \cdot r_{ci\alpha}}.$$

α runs over atoms in the molecule and $r_{ci\alpha}$ is the vector joining the i th molecular centre to the α th nucleus in the i th molecule. Here the angular-dependent molecular pair-correlation function $g(\mathbf{R}_{12}, \omega_1, \omega_2)$ is the function of interest, and \mathbf{R}_{12} is a vector from molecular centres one to two. This function has been simulated by Svishcher and Kusalik (1993), for example. Equation (2) has been written in the rigid-molecule approximation, which is appropriate for the low Q scale of interest here, and we are interested in the dominant Fourier component of the angular-averaged quantity in equation (2).

It has been pointed out in standard texts (e.g. Chandler (1987)) that the structure of water is determined mainly by the first coordination shell. For this reason the average nearest-neighbour intermolecular distance (d) controls the scale of the g functions. Similarly we expect the position (Q_0) of the dominant Fourier component to be related approximately to this scale by

$$2\pi/Q_0 \simeq d \tag{3}$$

provided the contribution of the angular-dependent scattering amplitudes F in equation (2) is not too large. It is known that at low Q this condition is met. Therefore a test is needed to demonstrate that Q_0 is low enough to meet this condition. Because the amplitudes F affect the different parts of the water molecule differently, such a test is provided by the comparison of peak positions of the three partial structure factors (figure 1), which should be the same when the above condition is met. The discussion of the previous section has shown this to be so at room temperature. However the functions of interest only vary slowly with temperature, which may be seen by comparisons of room-temperature and very-high-temperature data (see, e.g., Mountain (1989) for simulation data, and Buontempo *et al* (1992) or Postorino *et al* (1993) for experimental data). Therefore we expect this reasoning to be applicable over the smaller temperature range covered in our experiments. Moreover the above analysis is useful in showing the advantages of monitoring the system with a Q -space property rather than an r -space one.

3. Experimental details

The heavy-water sample was contained in a tubular 304 stainless-steel coil wound inside a thin-walled stainless-steel Dewar. It was calculated that the coil would burst at 4 kbar, and the highest pressure used in this experiment was 3.3 kbar. The dimensions of the coil were 3.5 cm diameter and 8.5 cm length; the stainless-steel tubing from which it was made was 1.6 mm o.d. and 1.2 mm i.d. Several coils were manufactured. After being wound, each coil was pressurized and depressurized five times, until the initial permanent deformations due to the pressure were unchanged on application of 3.3 kbar. The coils used in the experiment were further tested under pressure at 250 °C.

The temperature of the sample was varied by using the heaters at either end of the coil, and was closely controlled by passing heated argon gas through the centre of the spiral. A sketch of this assembly is shown as figure 3. It has the advantages of allowing a relatively large neutron beam to be used in a cylindrical geometry, and may be contrasted with the more conventional method of using single pressure tubes of limited area (see, e.g., Wu *et al* 1985). The sample assembly was mounted inside an argon envelope at the sample position

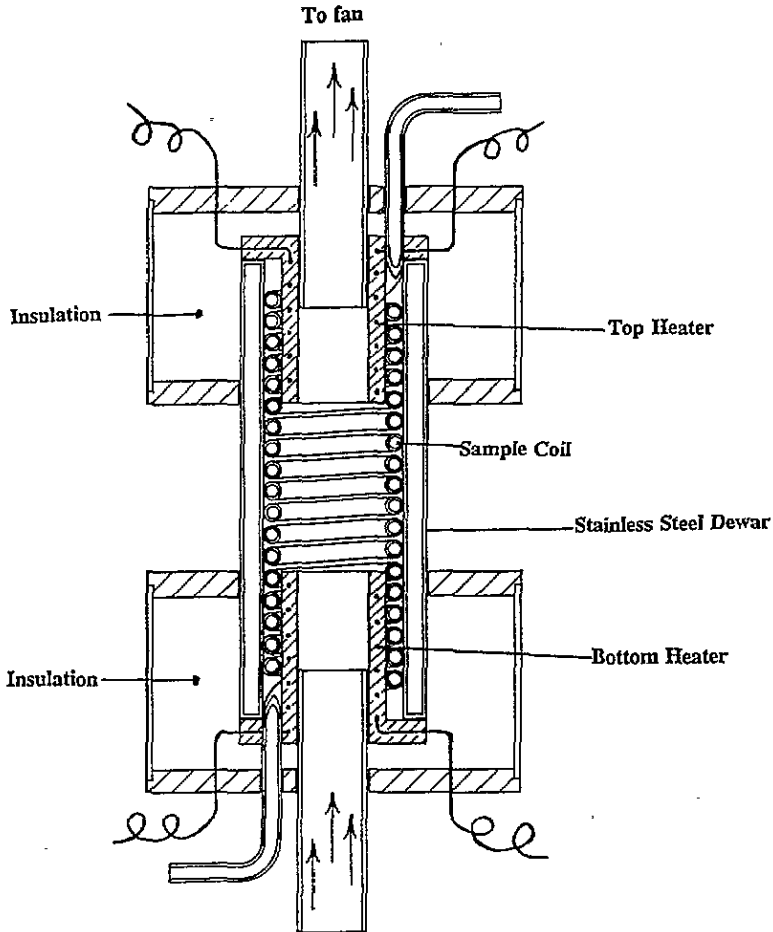
Table 1. A list of the states used in this experiment.

<i>T</i> (°C)	<i>P</i> (bar)	Difference from maximum density at 1 atm (1106 kg m ⁻³) (%)
-18	2300	10
-11	2380	10
-5	2430	10
0	2510	10
-11	1770	8
-5	1840	8
0	1890	8
5	1940	8
10	1980	8
20	2110	8
20	940	4
40	1125	4
60	1385	4
80	1700	4
11	1	0
24	39	0
61	350	0
78	570	0
100	950	0
126.5	1372	0
142	1678	0
110	120	-4
130	450	-4
150	810	-4
170	1170	-4
190	1550	-4
210	1925	-4
160	175	-8
180	520	-8
200	880	-8
220	1230	-8

of the GII neutron diffractometer (Egelstaff 1978) installed at the NRU reactor, Chalk River. The detectors of this instrument may be scanned automatically over a Q range covering the major features of $S(Q)$ for heavy water, using a wavelength of 0.24 nm.

With the sample container full of water, and at each of the pressures and temperatures shown in table 1, careful neutron-scattering scans were made. By adding several scans a statistical error of 0.3% was achieved. The third column of table 1 shows the constant densities chosen, which are expressed relative to the reference value of 1106 kg m⁻³. During the measurements the density and temperatures were typically held constant to $\pm 0.1\%$ and 1 °C respectively. Measurements taken with a vanadium reference sample and with an empty container, at several temperatures, were interspersed with the water measurements. Background data were taken with a cadmium mask over the beam.

An example of a single data scan, taken with the spiral empty and later full, is shown in figure 4, which demonstrates the favourable signal-to-background ratio with this sample assembly. After the states listed in table 1 had been measured, the data were reduced to the neutron structure factor $S(Q)$ by conventional procedures (see, e.g., Egelstaff 1987). Finally, from expanded plots of the structure factor over the region around 20 nm⁻¹ (see inset to figure 5) it was possible to determine the peak position (Q_0) accurately. In order



Heated Argon Gas

Figure 3. A cross-sectional view of the stainless-steel sample coil and its assembly inside a thin-walled stainless steel Dewar. The temperature of the coil was varied using the heaters at either end, and closely controlled by passing heated argon gas through its centre.

to relate the data in the way given by equation (3) the values of $2\pi/Q_0$ are plotted as solid circles in figure 5. Lines are drawn through the points to give a function of temperature for each density examined. Since the inter-relationships between the data points shown in the figure are of interest, the significant errors on these data are the random errors. For the quantity $2\pi/Q_0$ these errors are about $\pm 6 \times 10^{-4}$ nm. The systematic errors, which are related to the experimental calibrations and corrections, are several times larger. Several experimental groups have made measurements at 1 atm and a comparison of their absolute data illustrates the size of these errors—for example the data set of Gibson and Dore (1983) may be compared with that of Egelstaff and Polo (1986): there is a difference of about 3×10^{-3} nm between their estimates of $2\pi/Q_0$.

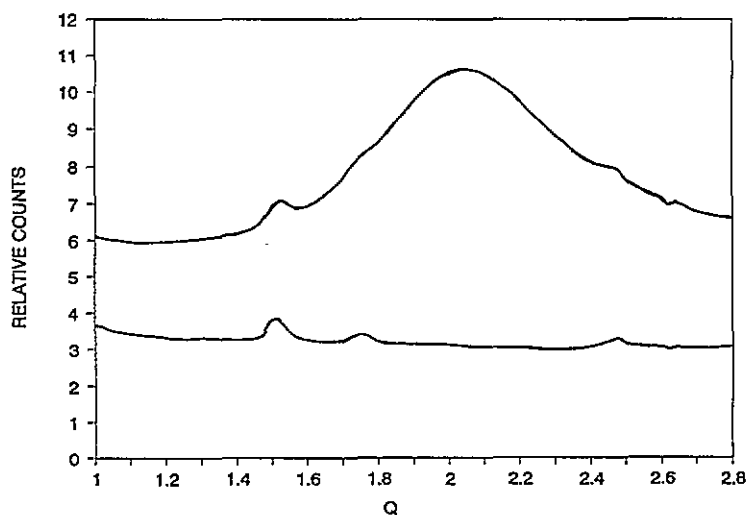


Figure 4. An example of raw neutron-scattering data from an empty spiral (lower curve), and the full spiral at +10% density (upper curve), to demonstrate the favourable signal-to-background ratio. The data are shown over the range of the major peak in $S(Q)$ only.

4. Discussion and conclusions

It is convenient to plot the reciprocal quantity $2\pi/Q_0$ as a function of temperature, for each of the six isochores studied, and this was done in figure 5. The reason is that this quantity is technically a suitable one for the purposes of a survey. It has the same magnitude as the intermolecular spacing (although it is not identical to it, see equation (3)) and, as discussed in section 2, can often serve as a monitor for this spacing. Several models were reviewed in section 2, and only one of them has the qualitative behaviour shown in figure 5. This was the atomic pair-potential model but, from figures 2 and 5, we see that $2\pi/Q_0$ shows for the model about half the fractional decrease with increasing temperature of that exhibited by water. This cannot be due to a softer intermolecular potential because water is relatively incompressible. Moreover this large effect is seen for all six of the isochores shown in figure 5, extending from -20 to 220°C . It is notable too that the experimental data have the opposite trend with temperature to that expected for the simple molecular model discussed in the background section. Such behaviour is expected for water if the structure changes from an open fourfold coordination to a closer and more random molecular arrangement as we move to higher temperatures along any of these isochores, rather than the types of structural rearrangement occurring in the model where increases in temperature reduce the relative importance to $S(Q)$ of the multipolar terms.

It is evident that the slopes of the lines drawn through the points in figure 5 vary with density. The low-temperature region (+8% and +10% in density) has only a few points, but it appears to involve a lower slope than that found in the liquid at +4%. For the higher-temperature data, the slope decreases gradually from the +4% case to the lower densities. This is perhaps, intuitively, to be expected. Buontempo *et al* (1992) report a single lower 'limiting value' for $2\pi/Q_0$ of 0.30 for $T = 523$ K on the coexistence curve. While they made only one measurement, it is clear that values on both sides of

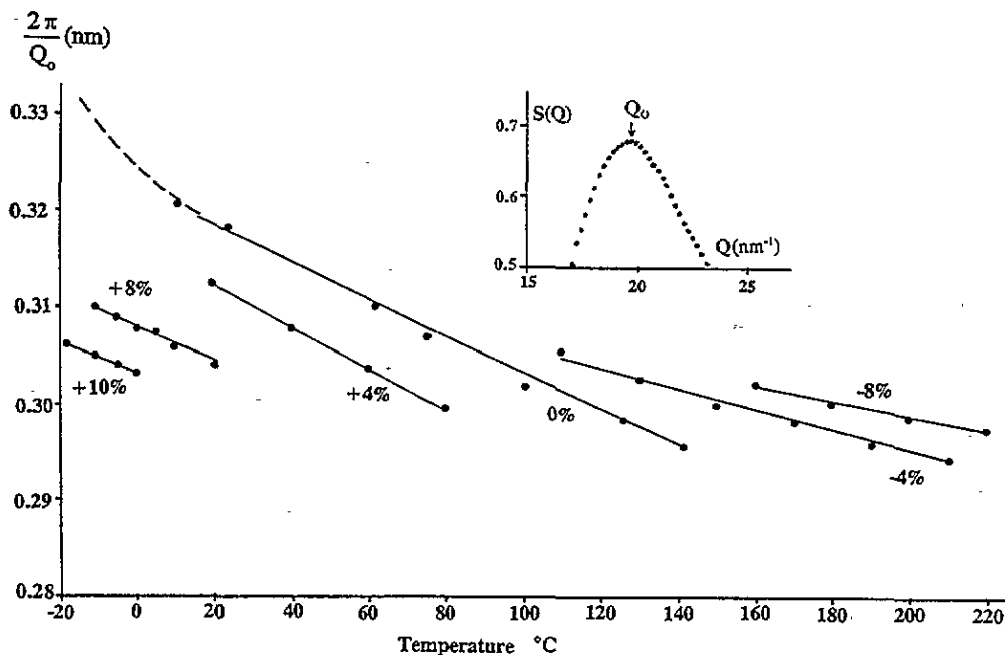


Figure 5. A plot of peak positions (see the inset) against temperature along several isochores. The percentages shown are greater or smaller than 1106 kg m^{-3} . The full lines are drawn to guide the eye. The dashed line is derived from the 1 atm of Bosio *et al* (1983) and of Egelstaff and Polo (1986). (A preliminary version of this diagram was presented (Egelstaff 1994) at the *European Physical Society Second Liquid Matter Conference*.)

their result are observed in our experiment, which demonstrates again the need for wide-ranging experiments covering a large part of the *PVT* diagram. On the other hand Bosio *et al* (1983) report values for supercooled water from -14.5 °C to higher temperatures. Since the density at 1 atm is within 1% of 1106 kg m^{-3} for temperatures between -20 °C and room temperature, we have combined the data of Bosio *et al* (1983) in the supercooled region with the data of Egelstaff and Polo (1986) for -1 °C to room temperature. The dashed line in figure 5 represents these combined data, which over this restricted temperature range may be compared to our 0% data. It is evident that this line slopes upward for temperatures lower than we used at this density, and therefore suggests that the linear behaviour shown by the full lines in figure 5 does not extend over a very wide range. Some indication of this behaviour may be evident in the -4% data also.

Wu *et al* (1982) report measurements of $S(Q)$ for some elevated temperatures and pressures. However, their data points are far apart and exact isochoric results cannot be extracted: nevertheless there is qualitative agreement with our data for the few overlapping results. A state in the supercritical range (at 400 °C and 640 kg m^{-3}) has been studied experimentally by Postorino *et al* (1993), who showed that the hydrogen bond peak in the OH pair correlation function had almost disappeared for that state. Thus one might anticipate that for data at higher temperatures and lower densities than shown in figure 5, the slopes of lines analogous to those in the figure could become positive.

In studying the isochoric temperature derivative of the structure factor for heavy water, Egelstaff and Polo (1986) suggested that the intermolecular distances might obey a scaling law. Their suggestion was that these distances might vary with temperature (at constant

density) as

$$\text{intermolecular distance} \sim (T - T_0)^{-n} \quad (4)$$

where T_0 is the reference temperature and n is an arbitrary index. They used $T_0 \ll T$, and in this case they found $n \sim 0.25$. This suggestion is roughly in agreement with the 4% data in figure 5, which covers a similar temperature range to their experiments. To obtain agreement at lower densities (e.g. -8%) would require a weaker variation with temperature such as $n \sim 0.1$, or a negative value for T_0 (e.g. -100 K). Therefore their model requires some further adjustment to cover our wider range.

Thus our data, summarized in figure 5, confirm and extend the overall picture given by the traditional model of water as outlined in the introduction. It is particularly interesting that these effects are observed over such a wide range, and show systematic trends over both density and temperature. In part this is due to the usefulness of the techniques employed. However, in order to achieve greater detail it will be necessary to make very precise partial-structure-factor measurements on light- and heavy-water mixtures and develop complete quantum corrections.

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