

Isochoric temperature differential of the x-ray structure factor and structural rearrangements in low-temperature heavy water

Louis Bosio

*Laboratoire de Physique des Liquides et Électrochimie,
Centre National de la Recherche Scientifique, 4 place du Jussieu, 75230 Paris Cedex 05 France*

Sow-Hsin Chen

*Department of Nuclear Engineering, 24-209, Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139*

José Teixeira

*Laboratoire de Physique Thermique, Centre National de la Recherche Scientifique,
Ecole Supérieure de Physique et Chimie Industrielle de la Ville de Paris,
10 rue Vauquelin, 75231 Paris Cedex 05 France*

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X-ray structure factors for heavy water were measured at temperatures of 40.0, 23.5, 15.5, 11.2, 7.1, 0.2, and -11.0°C . From these data isochoric temperature differentials (ITD) were constructed for pairs of temperatures $\Delta T = 40.0 - (-11.0) = 51.0$, $23.5 - 0.2 = 23.3$, and $15.5 - 7.1 = 8.4^\circ\text{C}$ around the maximum density point at 11.2°C . We show that the temperature dependence of the structural parameters can be obtained much more precisely from ITD than from the direct determination of the structure factor. A major structural rearrangement at the second-neighbor shell is identified from the interpretation of the ITD. We then interpret this rearrangement in terms of a possible increased molecular angular correlation of the tetrahedral structure at low temperatures.

I. INTRODUCTION

The structure factor of liquid water has been measured at different times with moderate accuracy both by x-ray^{1,2} and neutron-diffraction techniques.^{3,4} The x-ray structure factor can be shown to reflect mostly the molecular center of the oxygen local positional (O-O) correlations with a small admixture of O-D correlations, while the neutron structure factor contains major contributions from O-D and D-D correlations. In x-ray measurement corrections, multiple scattering, incoherent backgrounds, container contribution, etc., reduce the ultimate determination of the structure factors to an accuracy of perhaps a few percent. This kind of accuracy is not sufficient to detect the weak temperature dependence of the structural rearrangements in water as the temperature is reduced to the supercooled range.

In order to make more evident the variations of the structure factor $S(Q)$, where $Q = (4\pi/\lambda)\sin(\theta/2)$, λ is the wavelength of the radiation and θ is the scattering angle, and its derived quantity, the pair correlation function $g(r)$, a differential technique, was used by Dore and co-workers for treating their neutron-diffraction data.⁴

Indeed, if one uses $S(Q, T_{\text{ref}})$ of a reference temperature T_{ref} and compared it with $S(Q, T)$ at other temperature T , the Fourier transform of the differences $S(Q, T) - S(Q, T_{\text{ref}})$ will systematically give the small changes with temperature of the pair-correlation function. This method however does not avoid the treatment which normally must be applied to correct the data for density-dependent components. Fortunately, liquid water has the unique property of showing a maximum in the temperature-dependent density curve, and this feature offers a possibility for performing experiments at two different temperatures with the same density. Because many of the corrections are density dependent to the first order, they will cancel out in the evaluation of the difference

$$S(Q, \rho, T_1) - S(Q, \rho, T_2) \equiv \Delta S(Q, \Delta T),$$

where $\Delta T \equiv T_1 - T_2 > 0$ with T_1 and T_2 being two temperatures on each side of the density maximum for which the density is the same. This procedure was used recently by Egelstaff *et al.*⁵ to treat the temperature dependence of the neutron structure factor. This isochoric temperature differential (ITD) of the x-ray structure factor as we shall call it, offers a new and accurate technique for studying lo-

cal oxygen-atom ordering at low temperatures, as we shall show in the following paragraphs.

If we write

$$\Delta I(Q, \Delta T) \equiv I(Q, T_1) - I(Q, T_2) \propto \Delta S(Q, \Delta T), \quad (1)$$

where $I(Q, T)$ is the measured intensity at temperature T , then we can summarize advantages of this experimental procedure as follows.

(a) $\Delta I(Q, \Delta T)$ avoids complicated data correction procedure. (b) $\Delta I(Q, \Delta T)$ can be truncated in Q space at certain Q_{\max} without introducing significant truncation error in $\Delta g(r, \Delta T)$. This is because $\Delta I(Q, \Delta T)$ is very small for Q larger than Q_{\max} in spite of the fact that $S(Q)$ oscillates for much larger Q values. This feature, once verified, saves appreciable amount of measurement time. (c) The increased correlation of the second and third neighbors can be studied as temperature is lowered and (d) can be used as a critical test for theory of equilibrium structure of water and molecular-dynamic calculations based on *ab initio* potentials. (e) The temperature variation of the number of neighbors $\Delta N(R)$ up to a distance R from a central molecule can be obtained very accurately. Actually, this variation can be written as

$$\Delta N(R, \Delta T) = \rho \int_0^R \Delta g(r, \Delta T) 4\pi r^2 dr. \quad (2)$$

Moreover, this equation theoretically gives a way to normalize the data, because it can be written

$$\lim_{R \rightarrow \infty} \Delta N(R) = k_B \rho [T_1 \chi_T(T_1) - T_2 \chi_T(T_2)], \quad (3)$$

where χ_T is the isothermal compressibility, and k_B is the Boltzmann constant.

II. EXPERIMENTAL

The x-ray data were collected using a standard x-ray apparatus operating with a molybdenum tube ($\lambda = 0.7093 \text{ \AA}$). Monochromatization was obtained with a bent quartz monochromator in the incident beam, and experiments were run in the transmission mode. We used two kinds of sample holders: a plane-parallel holder 8 mm in thickness for experiments requiring low angle scattering and not too large supercooling, and a Lindemann glass tube with 3.8-mm inner diameter for experiments requiring large angle scattering or more extended supercooling. The use of both sample holders at the same pair of temperatures (i.e., 23.5/0.2°C) allows us to check that the corrected data are not affected by ex-

perimental conditions such as cell scattering, multiple scattering, etc.

Since structural differences for these temperature distances are weak, high accuracy measurement is required to interpret the data unambiguously. In order to minimize the effects of eventual drifts in either the x-ray generator or in the phonon counting electronics, we took the data alternatively on each side of the density maximum, so that 8×4000 counts were accumulated for intensity at each Q value. The diffractometer was operated in the step-scanning mode with steps of about 0.02 \AA^{-1} and angles from 2° to 72° , which corresponds to a Q range extending from 0.3 to 10.5 \AA^{-1} . A platinum resistor was used as a temperature sensing element to regulate T to within 0.1°C . Temperature was measured by a thermocouple immersed in the sample.

III. RESULTS AND INTERPRETATION

The molecular structure factor $S(Q, T)$ is related to the measured intensity $I(Q, T)$ by

$$S(Q) = \frac{K}{P(Q) \langle F(Q)^2 \rangle A(Q)} \times [I(Q, T) - A'(Q) I_{\text{cell}}(Q) - I_{\text{incoh}}(Q) - I_{\text{mult}}(Q)] - 1, \quad (4)$$

where K is a normalization factor, and $I_{\text{cell}}(Q)$, $I_{\text{incoh}}(Q)$, and $I_{\text{mult}}(Q)$ are the contributions from the cell, Compton, and multiple scattering. $\langle F(Q)^2 \rangle$ is the average scattered intensity from one independent molecule,¹ $A(Q)$ and $A'(Q)$ take into account the absorption of the sample and of the cell, and $P(Q)$ is the polarization factor. Since Narten and Levy¹ have shown that $\langle F^2 \rangle$ is nearly identical to $\langle F(Q)^2 \rangle$, the average scattering from a molecule of random orientation, in water, $S(Q)$ thus defined by Eq. (4), is the Fourier transform of pair-correlation function of molecular centers.

Because all the correction terms can be considered temperature independent, if one works at a fixed density, the differential $\Delta S(Q, \Delta T)$ is given by

$$\Delta S(Q, \Delta T) = \frac{K}{P(Q) \langle F(Q)^2 \rangle A(Q)} \times \Delta I(Q, \Delta T). \quad (5)$$

All the quantities in the prefactor are smooth and monotonous functions of Q and temperature independent. Since $\Delta S(Q, \Delta T)$ is related to $\Delta I(Q, \Delta T)$ by a multiplication factor which is a function of Q only, even though there is a slight error in computing this multiplication factor, the resulting Fourier

TABLE I. Molecular center structure factor $S(Q)$ of heavy water at the maximum density point $T=11.2^\circ\text{C}$ and the ITD of it $\Delta S(Q, \Delta T)$ at three pairs of temperature.

Q	$S(Q)$ ($T=11.2^\circ\text{C}$, $\rho=0.03328$ molecules \AA^{-3})	Q	$S(Q)$	Q	$\Delta S(Q, 8.4)$ $\rho=0.03327$	$\Delta S(Q, 23.3)$ $\rho=0.03323$	$\Delta S(Q, 51.0)$ $\rho=0.03308$
0.00		5.20	0.101	0.4	-0.0012	-0.0012	0.0076
0.08		5.28	0.079	0.5	-0.0002	0.0003	0.0070
0.16		5.36	0.053	0.6	-0.0009	0.0017	0.0078
0.24		5.44	0.026	0.7	-0.0007	0.0031	0.0106
0.32	-0.930	5.52	-0.001	0.8	0.0009	0.0029	0.0113
0.40	-0.930	5.60	-0.027	0.9	0.0008	0.0041	0.0142
0.48	-0.930	5.68	-0.053	1.0	-0.0006	0.0041	0.0146
0.56	-0.925	5.76	-0.076	1.1	-0.0014	0.0034	0.0152
0.64	-0.920	5.84	-0.095	1.2	0.0000	0.0000	0.0122
0.72	-0.915	5.92	-0.106	1.3	0.0025	-0.0038	-0.0024
0.80	-0.913	6.00	-0.109	1.4	0.0025	-0.0052	-0.0276
0.88	-0.903	6.08	-0.103	1.5	-0.0035	-0.0151	-0.0569
0.96	-0.897	6.16	-0.093	1.6	-0.0124	-0.0344	-0.0829
1.04	-0.883	6.24	-0.079	1.7	-0.0200	-0.0499	-0.0996
1.12	-0.860	6.32	-0.065	1.8	-0.0207	-0.0515	-0.1016
1.20	-0.828	6.40	-0.048	1.9	-0.0119	-0.0346	-0.0783
1.28	-0.790	6.48	-0.029	2.0	0.0023	-0.0010	-0.0224
1.36	-0.747	6.56	-0.007	2.1	0.0147	0.0369	0.0562
1.44	-0.688	6.64	0.014	2.2	0.0214	0.0632	0.1219
1.52	-0.604	6.72	0.034	2.3	0.0230	0.0728	0.1521
1.60	-0.487	6.80	0.049	2.4	0.0230	0.0699	0.1478
1.68	-0.339	6.88	0.059	2.5	0.0231	0.0627	0.1278
1.76	-0.178	6.96	0.065	2.6	0.0214	0.0537	0.1042
1.84	-0.030	7.04	0.068	2.7	0.0146	0.0364	0.0645
1.92	0.076	7.12	0.069	2.8	0.0019	0.0049	-0.0048
2.00	0.129	7.20	0.068	2.9	-0.0132	-0.0389	-0.0928
2.08	0.133	7.28	0.064	3.0	-0.0242	-0.0769	-0.1574
2.16	0.106	7.36	0.057	3.1	-0.0276	-0.0935	-0.1711
2.24	0.072	7.44	0.045	3.2	-0.0241	-0.0825	-0.1351
2.32	0.049	7.52	0.031	3.3	-0.0174	-0.0503	-0.0746
2.40	0.049	7.60	0.017	3.4	-0.0114	-0.0172	-0.0218
2.48	0.071	7.68	0.004	3.5	-0.0066	0.0053	0.0140
2.56	0.110	7.76	-0.007	3.6	-0.0017	0.0154	0.0344
2.64	0.159	7.84	-0.017	3.7	0.0039	0.0180	0.0420
2.72	0.214	7.92	-0.027	3.8	0.0088	0.0206	0.0425
2.80	0.265	8.00	-0.036	3.9	0.0112	0.0241	0.0397
2.88	0.302	8.08	-0.043	4.0	0.0105	0.0260	0.0369
2.96	0.313	8.16	-0.047	4.1	0.0080	0.0238	0.0347
3.04	0.287	8.24	-0.048	4.2	0.0057	0.0186	0.0307
3.12	0.224	8.32	-0.046	4.3	0.0046	0.0127	0.0246
3.20	0.133	8.40	-0.042	4.4	0.0042	0.0077	0.0184
3.28	0.030	8.48	-0.037	4.5	0.0036	0.0042	0.0139
3.36	-0.067	8.56	-0.030	4.6	0.0028	0.0013	0.0095
3.44	-0.145	8.64	-0.023	4.7	0.0023	-0.0015	0.0028
3.52	-0.196	8.72	-0.013	4.8	0.0020	-0.0040	-0.0062
3.60	-0.221	8.80	-0.003	4.9	0.0008	-0.0065	-0.0157
3.68	-0.226	8.88	0.005	5.0	-0.0019	-0.0093	-0.0234
3.76	-0.215	8.96	0.013	5.1	-0.0047	-0.0122	-0.0290
3.84	-0.196	9.04	0.019	5.2	-0.0079	-0.0140	-0.0319
3.92	-0.169	9.12	0.022	5.3	-0.0088	-0.0131	-0.0295
4.00	-0.139	9.20	0.024	5.4	-0.0074	-0.0095	-0.0227
4.08	-0.107	9.28	0.026	5.5	-0.0047	-0.0044	-0.0113
4.16	-0.074	9.36	0.027	5.6	-0.0020	0.0004	-0.0012

TABLE I. (Continued.)

Q	$S(Q)$ ($T=11.2^\circ\text{C}$, $\rho=0.03328$ molecules \AA^{-3})	Q	$S(Q)$	Q	$\Delta S(Q, 8.4)$ $\rho=0.03327$	$\Delta S(Q, 23.3)$ $\rho=0.03323$	$\Delta S(Q, 51.0)$ $\rho=0.03308$
4.24	-0.042	9.44	0.027	5.7	-0.0001	0.0029	0.0051
4.32	-0.011	9.52	0.026	5.8	0.0015	0.0035	0.0086
4.40	0.015	9.60	0.021	5.9	0.0030	0.0031	0.0109
4.48	0.040	9.68	0.013	6.0	0.0046	0.0027	0.0134
4.56	0.060	9.76	0.004	6.1	0.0044	0.0025	0.0150
4.64	0.077	9.84	-0.003	6.2	0.0033	0.0024	0.0151
4.72	0.092	9.92	-0.008	6.3	0.0018	0.0022	0.0130
4.80	0.105	10.00	-0.010	6.4	0.0002	0.0019	0.0094
4.88	0.116	10.08	-0.008	6.5	0.0001	0.0015	0.0029
4.96	0.123	10.16	-0.008	6.6	0.0000	0.0012	0.0000
5.04	0.124	10.24	-0.007	6.7	-0.0001	0.0008	-0.0030
5.12	0.117	10.32	-0.001	6.8	-0.0002	0.0006	-0.0041

transform of $\Delta S(Q, \Delta T)$ is a convolution of an accurate $\Delta g(r, \Delta T)$ with a slowly varying function in r . Thus small temperature variations in real-space data can be extracted with good accuracy.

We measured the scattered intensity $I(Q, T)$ for three pairs of temperature corresponding to temperature differences $T \equiv T_1 - T_2$ equal to $40.0 - (-11.0) = 51.0$, $23.5 - 0.2 = 23.3$, and

$15.5 - 7.1 = 8.4^\circ\text{C}$. We also measured the structure factor at the temperature of the density maximum (11.2°C) in order to scale the ITD curves and determine the constant K in the prefactor of Eq. (4).

Figure 1 gives the molecular structure factor $S(Q)$ at $T=11.2^\circ\text{C}$ and the corresponding pair-

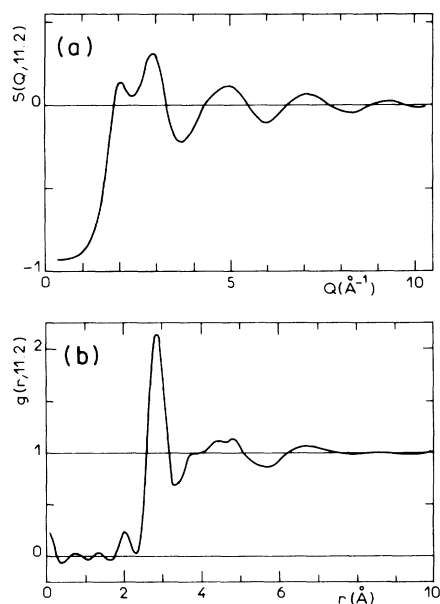


FIG. 1. Molecular center structure factor (a) and pair-correlation function (b) of D_2O at the temperature of maximum density (11.2°C). Note the oscillations in $S(Q)$ extending beyond 10\AA^{-1} and the important first structural peaks at 2.05 and 2.98\AA^{-1} . Pair-correlation function shows a well-defined first-neighbor peak at 2.9\AA , and a very broad second-neighboring peak around 4.8\AA ; the temperature variation of it is hard to quantify in a direct evaluation.

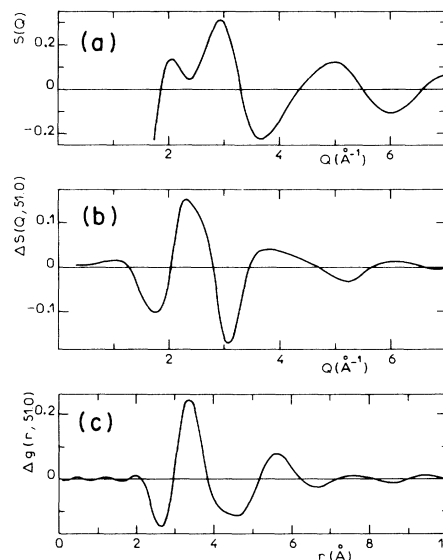


FIG. 2. (a) Same plot of $S(Q)$ as in Fig. 1(a) but truncated at 7\AA^{-1} , where the fluctuation of amplitude is still important. (b) ITD structure factor corresponding to the maximum temperature difference measured: $40.0 - (-11.0) = 51.0^\circ\text{C}$. Amplitude of oscillations is negligible beyond 7\AA^{-1} , and that portion of the graph is not shown here. This is in contrast to the behavior of the direct function $S(Q)$. (c) Differential pair-correlation function corresponding to (b). Interpretation of these curves is given in the text. They show that the distance between first and second neighbors is increasing with decreasing temperature and that the first shell is not strongly affected by temperature.

TABLE II. Molecular center pair-correlation function $g(r)$ of heavy water at the maximum density point $T=11.2^\circ\text{C}$ and the ITD of it $\Delta g(r, \Delta T)$ at three pairs of temperatures.

r	$g(r)$	$\Delta g(r, 8.4)$	$\Delta g(r, 23.3)$	$\Delta g(r, 51.0)$
0.1	0.234	0.0226	0.0074	-0.0019
0.2	0.118	0.0180	0.0030	0.0009
0.3	-0.003	0.0117	-0.0022	0.0038
0.4	-0.069	0.0055	-0.0062	0.0049
0.5	-0.060	0.0008	-0.0072	0.0035
0.6	-0.007	-0.0014	-0.0045	0.0000
0.7	0.039	-0.0010	0.0010	-0.0037
0.8	0.042	0.0012	0.0077	-0.0056
0.9	0.005	0.0041	0.0131	-0.0046
1.0	-0.033	0.0063	0.0155	-0.0010
1.1	-0.037	0.0069	0.0142	0.0034
1.2	-0.004	0.0059	0.0099	0.0061
1.3	0.034	0.0037	0.0045	0.0053
1.4	0.036	0.0013	0.0003	0.0010
1.5	-0.005	-0.0001	-0.0008	-0.0045
1.6	-0.051	0.0001	0.0018	-0.0081
1.7	-0.044	0.0015	0.0068	-0.0069
1.8	0.042	0.0035	0.0117	-0.0007
1.9	0.168	0.0046	0.0013	0.0077
2.0	0.249	0.0033	0.0083	0.0126
2.1	0.220	-0.0012	-0.0043	0.0073
2.2	0.101	-0.0089	-0.0236	-0.0127
2.3	0.012	-0.0184	-0.0465	-0.0471
2.4	0.110	-0.0277	-0.0679	-0.0898
2.5	0.486	-0.0341	-0.0823	-0.1295
2.6	1.079	-0.0353	-0.0852	-0.1528
2.7	1.692	-0.0301	-0.0742	-0.1486
2.8	2.086	-0.0187	-0.0496	-0.1115
2.9	2.112	-0.0029	-0.0148	-0.0449
3.0	1.794	0.0148	0.0249	0.0399
3.1	1.313	0.0308	0.0629	0.1260
3.2	0.890	0.0422	0.0933	0.1958
3.3	0.676	0.0471	0.1117	0.2360
3.4	0.684	0.0449	0.1159	0.2403
3.5	0.815	0.0367	0.1064	0.2112
3.6	0.944	0.0244	0.0859	0.1580
3.7	1.002	0.0109	0.0582	0.0941
3.8	0.997	-0.0013	0.0279	0.0320
3.9	0.981	-0.0106	-0.0013	-0.0192
4.0	0.996	-0.0161	-0.0262	-0.0556
4.1	1.044	-0.0185	-0.0452	-0.0784
4.2	1.094	-0.0184	-0.0579	-0.0916
4.3	1.117	-0.0174	-0.0646	-0.1001
4.4	1.111	-0.0164	-0.0663	-0.1069
4.5	1.098	-0.0161	-0.0639	-0.1125
4.6	1.099	-0.0163	-0.0584	-0.1152
4.7	1.118	-0.0163	-0.0504	-0.1121
4.8	1.133	-0.0154	-0.0404	-0.1009
4.9	1.121	-0.0128	-0.0288	-0.0808
5.0	1.074	-0.0083	-0.0160	-0.0532
5.1	1.009	-0.0023	-0.0027	-0.0216
5.2	0.949	0.0043	0.0102	0.0102
5.3	0.908	0.0103	0.0217	0.0383
5.4	0.887	0.0146	0.0308	0.0598

TABLE II. (Continued.)

r	$g(r)$	$\Delta g(r, 8.4)$	$\Delta g(r, 23.3)$	$\Delta g(r, 51.0)$
5.5	0.874	0.0165	0.0367	0.0734
5.6	0.863	0.0159	0.0388	0.0789
5.7	0.856	0.0130	0.0371	0.0772
5.8	0.865	0.0088	0.0320	0.0695
5.9	0.892	0.0043	0.0243	0.0571
6.0	0.932	0.0005	0.0154	0.0417
6.1	0.971	-0.0021	0.0064	0.0247
6.2	0.998	-0.0031	-0.0015	0.0079
6.3	1.014	-0.0029	-0.0074	-0.0069
6.4	1.025	-0.0019	-0.0110	-0.0185
6.5	1.038	-0.0006	-0.0124	-0.0257
6.6	1.054	0.0004	-0.0119	-0.0284
6.7	1.065	0.0008	-0.0101	-0.0270
6.8	1.065	0.0007	-0.0079	-0.0228
6.9	1.055	0.0001	-0.0056	-0.0170
7.0	1.041	-0.0006	-0.0035	-0.0109
7.1	1.031	-0.0012	-0.0019	-0.0056
7.2	1.027	-0.0015	-0.0005	-0.0013
7.3	1.025	-0.0015	0.0007	0.0019
7.4	1.019	-0.0013	0.0019	0.0042
7.5	1.008	-0.0009	0.0030	0.0060
7.6	0.994	-0.0005	0.0041	0.0073
7.7	0.986	-0.0002	0.0046	0.0081
7.8	0.985	0.0000	0.0046	0.0080
7.9	0.989	-0.0001	0.0037	0.0070
8.0	0.993	-0.0002	0.0018	0.0048
8.1	0.992	-0.0005	-0.0008	0.0016
8.2	0.988	-0.0007	-0.0038	-0.0022
8.3	0.986	-0.0011	-0.0066	-0.0061
8.4	0.988	-0.0014	-0.0087	-0.0096
8.5	0.995	-0.0017	-0.0097	-0.0121
8.6	1.001	-0.0019	-0.0096	-0.0131
8.7	1.003	-0.0021	-0.0084	-0.0125
8.8	1.000	-0.0020	-0.0061	-0.0103
8.9	0.995	-0.0017	-0.0033	-0.0067
9.0	0.992	-0.0011	-0.0001	-0.0022
9.1	0.993	-0.0004	0.0029	0.0023
9.2	0.996	0.0005	0.0052	0.0064
9.3	0.998	0.0012	0.0074	0.0094
9.4	0.997	0.0018	0.0084	0.0110
9.5	0.994	0.0022	0.0084	0.0112
9.6	0.992	0.0023	0.0079	0.0104
9.7	0.992	0.0022	0.0067	0.0087
9.8	0.996	0.0021	0.0052	0.0069
9.9	0.999	0.0019	0.0037	0.0050
10.0	1.002	0.0018	0.0021	0.0032

correlation function $g(r)$. It is to be observed that there are two characteristic peaks at around $Q_1=2.05$ and $Q_2=2.98 \text{ \AA}^{-1}$ with oscillations extending beyond $Q=10 \text{ \AA}^{-1}$. If these oscillations are not properly taken into account, the resulting Fourier transform will produce spurious effects in $g(r)$, especially in the low- r region. It can be seen

from Fig. 1(b) that the positions of the second neighbors are not very well defined, not to mention its temperature dependence. Tables I and II summarize the numerical data for $S(Q, 11.2^\circ\text{C})$ and $g(r, 11.2^\circ\text{C})$, respectively.

In Fig. 2(a) we show again for reference $S(Q, 11.2^\circ\text{C})$ in a truncated form and Figs. 2(b) and

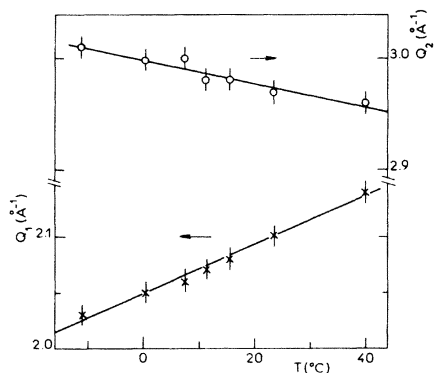


FIG. 3. Position of the first and second structural peaks in $S(Q)$ vs temperature showing that they move in an opposite direction almost linearly with temperature. This figure is helpful for the interpretation given in Fig. 2(b).

2(c) differentials $\Delta S(Q, \Delta T)$ for $\Delta T = 51.0^\circ\text{C}$, as well as its Fourier transform $\Delta g(r, \Delta T)$. In Fig. 2(b), the first oscillation, from a negative peak at 1.8 \AA^{-1} to a positive peak at 2.2 \AA^{-1} , corresponds to a shift of the first peak in $S(Q)$ towards the lower- Q region when temperature is decreased, while the second oscillation from the positive peak at 2.2 \AA^{-1} to a negative peak at 3.1 \AA^{-1} corresponds to a shift of the second peak in $S(Q)$ towards the higher- Q region always when temperature is decreased. Moreover, comparing the amplitudes of the oscillations, one can deduce that the second peak in $S(Q)$ is increasing in amplitude with decreasing temperature. Figure 3, which was obtained from the direct evaluation of $S(Q)$, shows the shifts of the two peaks more clearly.

It is remarkable that, within the accuracy of our experiments, there is no significant change of the structure factor beyond 7 \AA^{-1} . Actually, our measurements extend only until 10.5 \AA^{-1} . However, even allowing for some nonzero contribution to $\Delta S(Q)$ above 10.5 \AA^{-1} , the resulting Fourier transform will not affect the intermolecular part of the structure factor significantly.¹ This feature implies that the first coordination shell is less strongly affected by the temperature variation than farther neighbors' shells. This result can be seen also in the real-space function [Fig. 2(c)]: The first oscillation around the position of the first neighbor at 2.8 \AA has a smaller amplitude than what would be expected if the temperatures were to affect uniformly all neighbors, because the uniform effect would have produced oscillations decreasing in amplitude starting from the first one. A practical consequence of the above observation is that $\Delta S(Q, \Delta T)$ need only be measured until $Q_{\text{max}} \approx 7 \text{ \AA}^{-1}$ without losing information in the Fourier transform.

A second conclusion which can be drawn from Fig. 2(c) is that the important rearrangement of the molecular centers occurs at the second-neighbor shell as temperature is varied. Actually, an interpretation of the water structure must take into account the dynamic properties of the liquid. Many assumptions have been done in connection with the hydrogen-bond angles and their temperature dependence.⁶ It is well known that x-ray radiation cannot give any direct information either on dynamics or molecular orientational correlations. Nevertheless, it can be concluded from our r -space data that the second nearest neighbors have a tendency to move away when the temperature is lowered. This corresponds to an increase of the O-O-O angle towards the optical tetrahedral coordination value of 109.5° . This feature in experimental data confirms a hypothesis very often made in the literature⁷ that molecules which are hydrogen bonded, which are present in larger number at low temperatures, are surrounded by larger free volume than those molecules less bonded to their neighbors. It is worth noting, especially referring to molecular-dynamic simulations, that a good measure of the number of neighbors of a given molecular species must extend at least to the second neighbor. Indeed, as we have seen, the first coordination shell is not strongly affected by the temperature. This is a manifestation that O-O-O angular correlations are at the origin of the density fluctuations^{8,9} and, consequently, also of the thermal anomalies of water.

A confirmation of this can be seen clearly if one plots variation of the number of neighbors given by

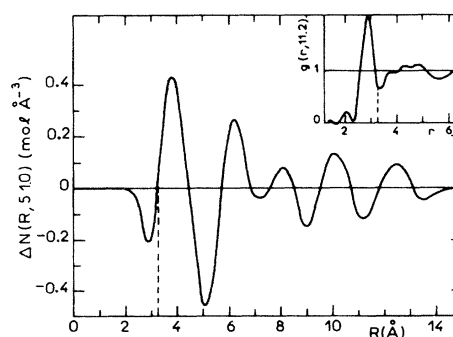


FIG. 4. Variation of the number of molecular centers within a distance F from a central molecule for the largest measured temperature interval showing that temperature variation has smaller effects in the first shell than in the further shells, a feature which is interpreted as originated from increased O-O-O angular correlations when temperature is decreased. The insert shows $g(r)$ at 11.2°C for reference.

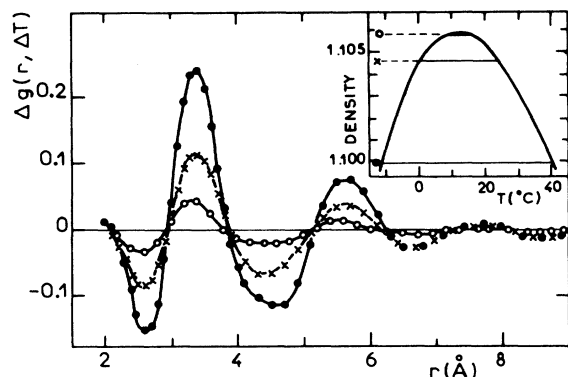


FIG. 5. $\Delta g(r, \Delta T)$ for the three measured pairs of temperature. Amplitude of the oscillations is proportional to ΔT within the experimental error. These three curves can be collapsed in one single curve if we plot instead $\Delta g(r, \Delta T)/\Delta T$ vs r . Insert shows the density curve and the position of the measured temperatures.

Eq. (2). This curve is shown in Fig. 4 for the largest measured $\Delta T = 51.0^\circ\text{C}$.

At around $R = 3.2 \text{ \AA}$ [which corresponds to integrating $g(r)$ up to the first-neighbor shell] we see that although their distances are slightly contracted, the number of first nearest neighbors is not significantly affected. However, differences are more noticeable beyond the first shell, showing clearly the "creation" of empty space between the first-, second-, and third-neighbors' positions.

We note incidentally that $\Delta N(R \rightarrow \infty)$ as given by Eq. (3) although theoretically gives a way to normalize the data, in practice, the accuracy in $\Delta g(r, \Delta T)$ at large r is not sufficient for this purpose.

A last feature of our results can be seen in Fig. 5 where we plotted the differences $\Delta g(r, \Delta T)$ for the three measured pairs of temperatures. Within the experimental accuracy, the three curves have identical shape and have a smooth and linear temperature dependence. This feature suggests that, in spite of the strong thermodynamic anomalies at low temperatures,¹⁰ at the microscopic level the "buildup" of the structure is done in a rather smooth way.

It would be interesting to test the temperature

dependence of the limit in r above which $\Delta g(r, \Delta T)$ is negligible. In principle, this limit could be related with the connectivity length of the hydrogen-bond network, but, because it changes drastically only in the deep supercooled region, we would not expect any detectable effect in our data.

IV. CONCLUSION

We have shown that measurements of the ITD's of the x-ray structure factor is a very powerful technique for structural study of water, both in normal and in supercooled states. The ITD can be measured with much higher precision than the structure factor itself. The main reason is that most of the difficulties connected with various corrections can be largely overcome.

In this work we have, among other things, given the temperature dependence of the number of neighbors up to a certain distance R at constant densities. From this observation, we deduce that the O-O-O angular correlation increases with decreasing temperature tending toward building up of a tetrahedral network. These results can, in the future, be compared and used as a test for accuracy of different molecular-dynamic calculations. For this purpose, we give in Tables I and II numerical data for both $\Delta S(Q, \Delta T)$ and $\Delta g(r, \Delta T)$ for the three pairs of temperatures. $S(Q)$ and its Fourier transform $g(r)$ at 11.2°C are also given in Table I as references. Although the precision of the $S(Q)$ given is better than 1%, considering the uncertainty in data corrections and normalization the absolute accuracy of $S(Q)$ should be put at several percent, as is also true for all other $S(Q)$ data published in the literature.

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