Hydrogen-Hydrogen Pair Correlation Function in Liquid Water

A. K. Soper and R. N. Silver
Los Alamos National Laboratory, Los Alamos, New Mexico 87545

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The hydrogen pair correlation function of liquid water has been measured by time-of-flight neutron diffraction. The isotope substitution technique has been used to cancel the problematic hydrogen incoherent and inelastic scattering without introducing a dynamical model of the liquid. The results are in remarkable agreement with computer simulations of water using model potentials, although the short-range structure is more tightly coordinated than predicted.

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The structure of water is of obvious chemical and biological interest, as well as of fundamental importance as a strongly hydrogen-bonded liquid. To determine specific atom-atom correlation functions in water requires three diffraction measurements in which the relative scattering amplitudes of the components are varied. Only a neutron scattering experiment using hydrogen isotope substitution has sufficient sensitivity to extract the H-H correlation function. However, hydrogen suffers considerable recoil in a neutron collision which makes interpretation of the diffraction experiment difficult. Previous studies of water have introduced models for the inelastic scattering.[1]

In this paper, we report a model-independent determination of the H-H correlation function in water. First, the experiment was performed at a pulsed neutron source. The incident energy, as measured by time of flight, was variable and the fixed scattering angle was small to minimize inelasticity effects. Second, the data analysis invoked a formal cancellation of the self-scattering in the linear combination of data from isotope-substituted samples to obtain the H-H correlation function, as demonstrated in a recent experiment on liquid hydrogen chloride.[2] The validity of this cancellation for water requires an additional assumption to account for H-D exchange as discussed in detail below.

The quantity sought in a diffraction experiment is the static structure factor $S(Q)$. Following Van Hove,[3] it is usual to split the structure factor into a "self" term, $S_\alpha{}^s$, corresponding to scattering from single atoms, and a "distinct" term, $S_{\alpha\beta}{}^d$, corresponding to interference scattering between distinct atoms. For an N-component system the total structure factor is

$$S(Q) = \sum_{\alpha}^{N} n_\alpha \langle c_\alpha{}^2\rangle S_\alpha{}^s(Q) + \sum_{\alpha\beta}^{N} n_\alpha n_\beta \langle a_\alpha\rangle\langle a_\beta\rangle S_{\alpha\beta}{}^d(Q), \qquad (1)$$

where $c_\alpha{}^2$ is the sum of the squares of the coherent scattering length, a_α, and the incoherent scattering length, and n_α is the number of atoms per molecular unit, for atomic species α. The angular brackets indicate averages over the isotopes of each nucleus. The isotopes are assumed to be randomly distributed which is certainly valid for heavy and light water because of the rapid proton/deuteron exchange.

The quantity measured in a diffraction experiment is not $S(Q)$, but a time-of-flight differential cross section $\Sigma(Q)$ at a fixed angle which is given by

$$\Sigma(Q_e) = \int_{-\infty}^{\infty} d\omega \frac{k_f}{k_i} S(Q,\omega) I(k_i) E(k_f) \left(\frac{\delta k_i}{\delta k_e}\right)_\omega . \qquad (2)$$

Here k_i and k_f are initial and final neutron wave vectors, ω is the energy transfer, Q_e is the momentum transfer for elastic scattering corresponding to the total time of flight, and $I(k_i)$ and $E(k_f)$ are the neutron spectrum and detector efficiency normalized to their values at the elastic wave vector k_e. $S(Q,\omega)$ is the dynamic structure factor whose integral over ω at constant Q yields the desired quantity $S(Q)$. From (2), it is clear that $\Sigma(Q)$ is equal to $S(Q)$ only in the limit of no inelastic scattering, $S(Q,\omega) = S(Q)\delta(\omega)$. A general method of calculating corrections to $\Sigma(Q)$ to determine $S(Q)$ for heavy atoms has been developed as a series expansion by Placzek.[4] For light atoms such as hydrogen the method is impractical because a large number of terms are important which must be calculated from a model for $S(Q,\omega)$. The inelasticity corrections are much larger for the self terms in (1) than for the distinct terms, as the self terms sample all atomic motions while the distinct terms sample only collective motions. Finally examination of the kinematics shows that the corrections can be minimized by scattering at small angles and large k_i to achieve a desired Q.

In our time-of-flight experiment, we performed measurements on three isotopically substituted samples: H_2O, D_2O, and an $H_2O{:}D_2O$ mixture. Using (1) with $\Sigma(Q)$'s substituted for $S(Q)$'s, one can then show that

$$x\Sigma^{H_2O}(Q)+(1-x)\Sigma^{D_2O}(Q)-\Sigma^{H_2O:\,D_2O}(Q) = 4x(1-x)(\langle a_H\rangle-\langle a_D\rangle)^2\Sigma_{HH}{}^d(Q)+\Delta \qquad (3)$$

under the usual assumption that distinct structure factors are invariant to isotope substitution. The quantity x is the proportion of light water in the mixture. Equation (3) is similar to the second-order difference technique of Enderby and Neilson[5] to remove self scattering. It is applied here for the first time to a low-angle time-of-flight experiment on light elements. When combined with the high epithermal flux of a pulsed source, the Weapons Neutron Research facility at Los Alamos (WNR), the inelasticity corrections to the distinct scattering are minimized. The main inelasticity contribution to $\Sigma_{HH}{}^d$ arises from the intramolecular function and we estimate this later.

Contributions to the term Δ arise from noncancellation of inelasticity effects in the self terms and in the O-H and O-D distinct terms. We make the assumption that the isotopic composition of surrounding molecules is not important to the determination of the Σ's for a given molecule. Then the only contribution to Δ arises from H-D exchange. The largest term, which comes from hydrogen self scattering, is

$$\Delta_H = 2x(1-x)[c_H{}^2(\Sigma_H{}^{s,H_2O}-\Sigma_H{}^{s,HDO})+c_D{}^2(\Sigma_D{}^{s,D_2O}-\Sigma_D{}^{s,HDO})]. \qquad (4)$$

Here $\Sigma_H{}^{s,H_2O}$ is the hydrogen self cross section for the H_2O molecule. We have calculated Δ_H in the only model susceptible to analysis: the freely translating and rotating molecule. Using the formalism of Rahman,[6] we determined the Σ's under the present experimental conditions (scattering angle = 40°, incident flight path = 10 m, scattered flight path = 1 m) along the same lines as described previously.[7] The results show that $|\Delta_H| \leq 0.025$ b/molecule over the Q range of interest and is slowly varying with Q. The contributions to Δ_H are the rotational excitations, which are hindered in the liquid state. An equivalent analysis was developed for the oxygen self scattering and for the O-H distinct scattering and the corresponding contributions to Δ were found to be much smaller. We, therefore, make the *Ansatz* in the subsequent analysis that Δ can be ignored for liquid water.

The experiment used the general-purpose diffractometer[8] at WNR. The differential cross sections of liquid water were measured at a temperature of 25 °C and a pressure of 0.78 atm. Samples were contained in a thin-walled flat-plate aluminum container and the sample thickness was 0.34 mm for H_2O and 3.3 mm for D_2O. The small thickness ensured that the multiple scattering never exceeded 25% and averaged about 15%. The data were corrected for multiple scattering and attenuation and normalized to the scattering from a vanadium standard sample. Typical counting times were three days per sample and yielded counts on the order of 10^6 at the peak of the incident spectrum, after combining data from sixteen proportional counters and binning in increments of Q of 0.1 Å^{-1}. Sample thickness was monitored to about 3% by transmission detectors placed before and after the sample.

The measured cross sections are shown in Fig. 1. We observe that the cross sections are almost flat in the range 15–20 Å^{-1} and close to the static limit. Measurements at 90° and 150° show much larger deviations from the static limit. This confirms the smallness of the inelasticity effects at low angles. The D_2O curve shows excellent agreement in peak heights and positions with reactor data.[9] However, the inelasticity "droop" present in the reactor experiment is negligible here and the data extend to a much larger Q value of 30 Å^{-1}. A lower Q limit of 1.4 Å^{-1} is present in the data because of frame

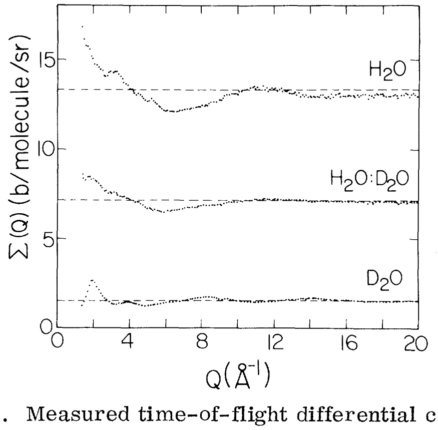

FIG. 1. Measured time-of-flight differential cross sections for light water, heavy water, and a 50:50 mixture of heavy and light waters. The dashed lines correspond to the static limit for the self terms.

overlap at WNR which occurs at 8.3 msec on a total flight path of 11 m.

The analysis of Eq. (3) was applied directly to the three data sets. This yielded a result averaging 0.5 b/molecule for $Q < 12$ Å^{-1}. To obtain the H-H structure factor shown in Fig. 2 a 4.1% normalization correction [chosen to minimize structure in $g_{\mathrm{HH}}(r)$] to the H$_2$O data set was applied. This is within the combined experimental uncertainties in sample-thickness, multiple-scattering, and attenuation corrections for the three samples. A significant amount of structure emerges in the region 1.4–12 Å^{-1}, with the structure obscured by poor statistics at higher Q. The data are compared to the predictions of two computer simulations, the first due to Lie, Clementi, and Yoshimine (LCY),[10] and the second using the ST2 potential due to Stillinger and Rahman.[11] To produce the curves shown, we calculated the $S_{\mathrm{HH}}{}^d(Q)$ from the simulated $g_{\mathrm{HH}}(r)$ and added the $S_{\mathrm{HH}}{}^d(Q)$ from the free-molecule calculation mentioned earlier. The data and simulations essentially agree for $Q > 4$ Å^{-1}, but only the LCY potential reproduces the peak around 1.9 Å^{-1} although at too large a Q value.

The $S_{\mathrm{HH}}{}^d(Q)$ shown in Fig. 2 is related to the radial distribution function by Fourier transform. Because of the limited Q range over which the statistics are good, we have calculated the transform

$$g_{\mathrm{HH}}(r) = 1 + \frac{1}{2\pi^2\rho}\int_0^{10.8\,\text{Å}^{-1}} \Sigma_{\mathrm{HH}}{}^d(Q)\,Q^2\,\frac{\sin(Qr)}{Qr}\,dQ\,, \qquad (5)$$

where the $S_{\mathrm{HH}}{}^d(Q)$ from 0 to 1.4 Å^{-1} has been extrapolated to the compressibility limit by a straight line. Again the agreement between simulations and experiment as shown in Fig. 3 is good. However, the intramolecular peak at 1.5 Å is too broad on the basis of vibrational zero-point motion (rms amplitude 0.09 Å). This may in part be due to the premature truncation of the integral at 10.8 Å^{-1}. It may also be due to a significant inelasticity correction to the distinct H-H function. To test both possibilities we transformed the $\Sigma_{\mathrm{HH}}{}^d(Q)$ from the free-molecule calculation in the same fashion as Eq. (5) using a H-H distance of 1.489 Å. The width and peak position of the calculated intramolecular peak agree well with the data. The inelasticity correction shows up primarily as a second peak (not shown here) at an unphysical value of 0.8 Å, which indeed is also present in the measured $g(r)$. The data suggest a slightly smaller intramolecular peak position, 1.48 Å, in the liquid than in the free molecule, but clearly the truncation in Eq. (5) prevents any definitive conclusions on intramolecular distances.

For the intermolecular distribution the first peak is shifted to slightly smaller radius compared to either simulation, as is the second peak, and the first minimum is deeper. The coordination number of the first peak, calculated to a radius of 3.1 Å, is 5.7 hydrogen atoms compared

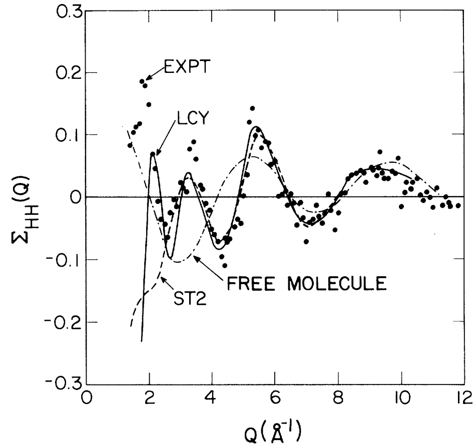

FIG. 2. H-H partial structure factor obtained directly from Fig. 1 (dots) compared to the simulations of LCY (Ref. 10) (continuous line) and ST2 (Ref. 11) (dashed line). The data beyond 12 Å^{-1} are not shown because of the poor statistical accuracy in that region. The simulations have a function corresponding to the single-molecule scattering added to them, shown as a dash-dotted line.

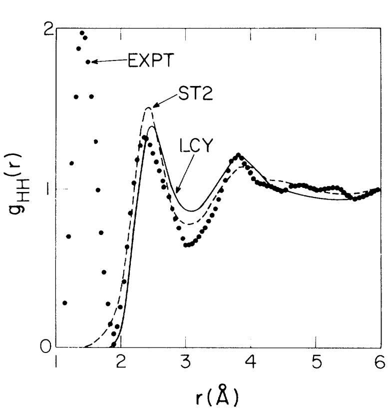

FIG. 3. H-H pair radial distribution function obtained by Fourier transform after truncating the data from Fig. 2 at 10.8 Å^{-1}. Other notation as in Fig. 2.

to 6.1 for the LCY simulations and 6.5 for the ST2 calculation. This slightly smaller value and the deeper minimum between the intermolecular peaks imply that the near-neighbor shell of molecules is more tightly coordinated than the simulations predict. Other physically plausible ways of extrapolating between 0 and 1.4 Å^{-1} in Eq. (5) result in smaller coordination numbers and deeper minima than the straight-line approximation. A similar picture emerges from an analysis of the O-H distinct structure factor data, to be reported elsewhere. These yield a hydrogen coordination number of 1.7 about oxygen in good agreement with the LCY simulations.

In conclusion, using the high epithermal flux of a pulsed neutron source and a novel isotope-substitution technique, we have obtained the first model-independent distinct structure factors in liquid water. The results are in good agreement with simulations, but they suggest that the short-range order is more tightly coordinated than predicted by available theories. This method should also be applicable to many other systems with light atoms where inelasticity corrections are significant.

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Channeling Radiation from Relativistic Positrons in LiF

B. L. Berman
Lawrence Livermore National Laboratory, University of California, Livermore, California 94550

and

S. Datz and R. W. Fearick[(a)]
Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

and

J. O. Kephart, R. H. Pantell, H. Park, and R. L. Swent
Department of Electrical Engineering, Stanford University, Stanford, California 94305

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Unusual features of radiation spectra from relativistic positrons channeled in the ionic crystal LiF have been observed.

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We have observed channeling radiation from a binary crystal, in this case from relativistic positrons channeled in the ionic crystal LiF. Some of the features of this channeling radiation are unusual and interesting because of the presence and periodicity of two different ionic species of widely different atomic number (Li, $Z = 3$, and F, $Z = 9$). Along the planes whose Miller indices are all odd (or along axes whose Miller indices sum to an even number) the Li and F ions are