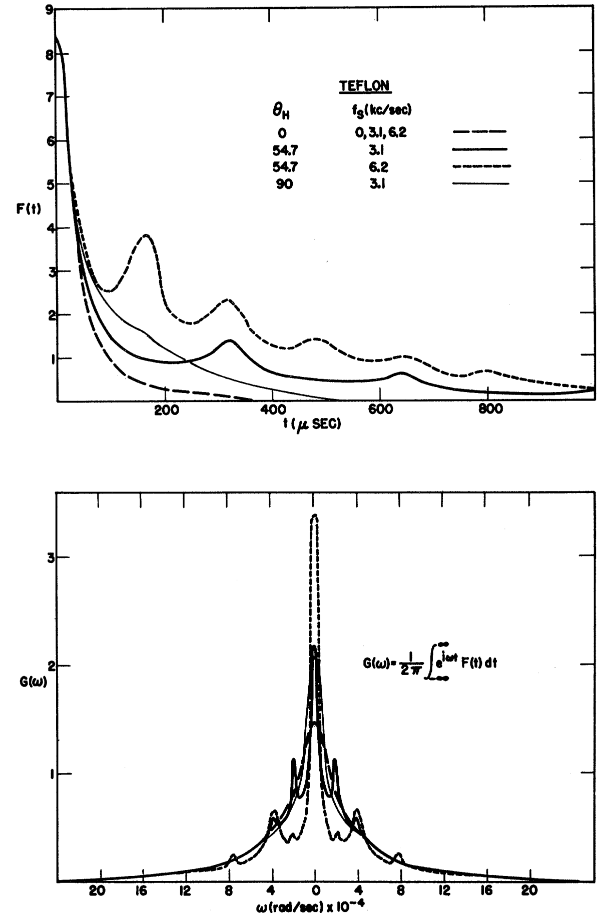

FIG. 2. Free induction decays for spinning and nonspinning samples of Teflon and their Fourier transform. The curves are corrected for instrumental nonlinearities.

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DIFFUSIVE MOTIONS IN LIQUIDS AND NEUTRON SCATTERING

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Measurements of neutron inelastic scattering by a classical liquid provide access to the details of the atomic motions in the liquid, by way of time-dependent correlation functions introduced by Van Hove.[1] The author has discussed some features of these correlation functions in connection with a series of experiments[2] on the isotopic pair–light water which scatters incoherently, and heavy water which scatters coherently. These functions have also been discussed by Vineyard.[3] The partial differential neutron scattering cross sections are Fourier transforms over space and time of the time-dependent correlations,[1] and essentially are functions only of neutron energy transfer and momentum transfer, i.e., of $\omega = \hbar^{-1}(E_0 - E')$ and $\vec{Q} = \vec{k}_0 - \vec{k}'$, where E_0, E', $\vec{k}_0$, $\vec{k}'$ are, respectively, the ingoing and outgoing neutron energies and wave vectors. The coherent cross sections are determined by the pair correlation function, which classically is "the probability that, given an atom at position zero at time zero, any atom is at position $\vec{r}$ at time t." The incoherent cross sections are determined by the self-correlation function, which classically is "the probability that, given an atom at position zero at time zero, the same atom is at position $\vec{r}$ at time t."

The experiments[2] led to the conclusion that the qualitative behavior of the cross sections is largely determined by the asymptotic behavior of the correlation functions at very small times and at large times. Because the correlation functions for any system (solid, liquid, or gas) change very rapidly at small times, the scattering contains an inelastic component which, for a classical system at a given large Q, is almost independent of the state of the system, being determined by the temperature and by the mass of the atoms. At long times, in a nondiffusing solid, the correlation functions become independent of time and hence the scattering contains an elastic component, which is the Fourier transform of the time-independent structure. For coherent scattering this elastic component consists of Bragg peaks whose intensity is modulated by the Debye-Waller form·factor of the (Gaussian) "thermal cloud" of an individual atom. For incoherent scattering the intensity of the elastic component is everywhere proportional to the Debye-Waller form factor. In liquid water it was found that a quasi-elastic component of the scattering exists, which for coherent scattering is correlated with the liquid diffraction peak thus showing interference effects,[4] and which for incoherent scattering has intensity proportional to a somewhat non-Gaussian form factor. These facts were interpreted as showing that in a liquid, as in a solid, a "thermal cloud" is quickly set up, the process of setting it up generating the inelastic component of the scattering, but that in a liquid the "thermal cloud" is non-Gaussian. Thereafter the cloud changes only slowly by diffusive processes, the changes in time being reflected in the small energy transfers which actually occur in the quasi-elastic component. The details of these energy transfers, as functions of Q, give information on the way diffusion occurs. The measurements could not be reconciled with the simple models of diffusion by large jumps only (activation diffusion), or of diffusion by small motions only (continuous diffusion).

With the resolution available for the earlier experiments, the energy broadening of the quasi-elastic component, from which the above deductions on the nature of the diffusive motions in liquids were made, was just barely detectable in the most interesting region of Q. Measurements have now been made at much higher resolution

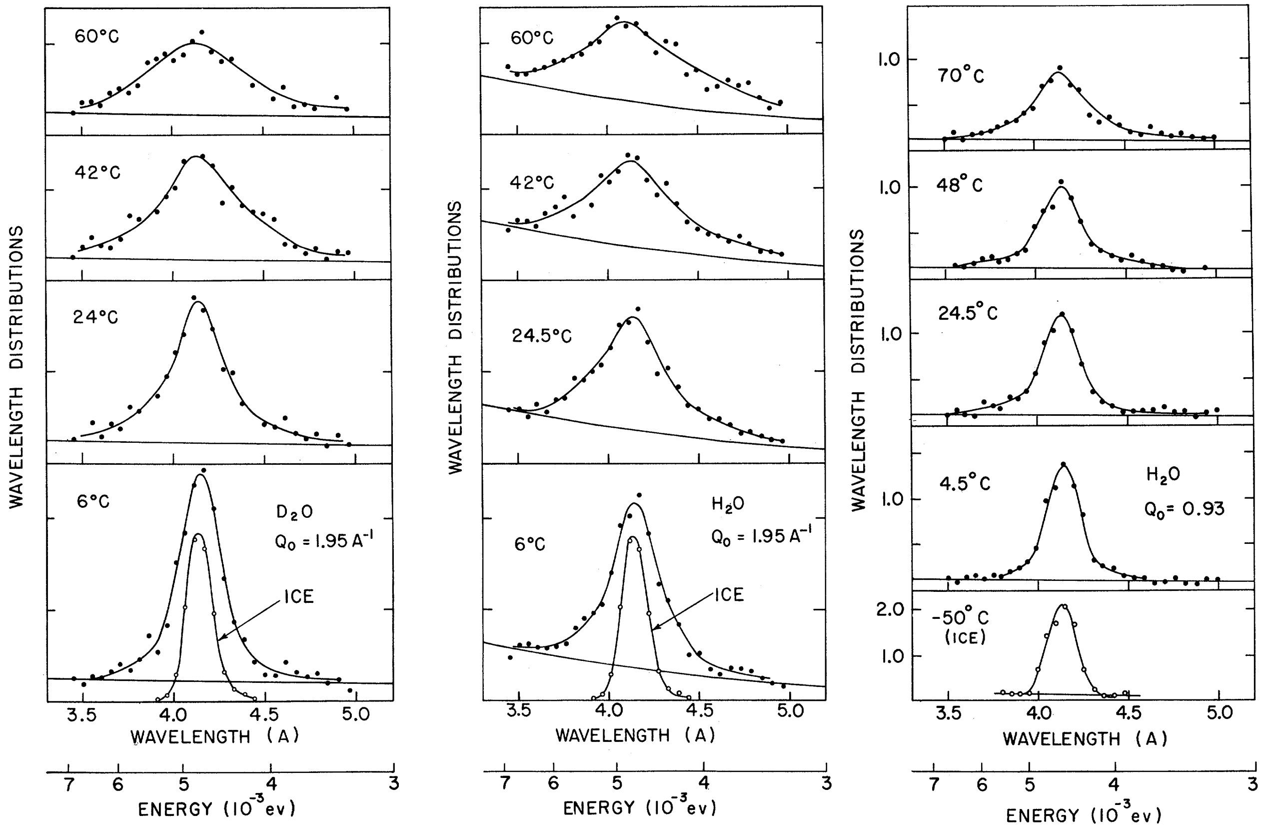

FIG. 1. The wavelength distributions of 4.15A neutrons scattered through angles $\phi = 80°$ and 36°, by light and heavy water at several temperatures. $Q_0 = (4\pi/\lambda_0)\sin(\phi/2)$. Similar measurements on H_2O ice, which give the resolution function, are also shown. The mean peak of the diffraction pattern for D_2O occurs at about $Q_0 = 1.95$ (see reference 2).

with the new rotating crystal spectrometer (at the NRX reactor), briefly described elsewhere.[5] Neutrons of incident wavelength 4.15 A were scattered from fairly thin (~0.3 mean free path) specimens of light and heavy water at angles of 80° and 36°, and the times of flight of scattered neutrons with energies near the initial energy were measured in a 30-channel timesorter. By correcting for counter sensitivity and for frame overlap,[6] the distributions in wavelength shown in Fig. 1 were obtained. The resolution function, obtained from similar measurements on ice, is also shown. The curves represent the quasi-elastic component superposed on the central part of the inelastic component. The inelastic component for H_2O was taken to be the shape of a mass-18 gas distribution, fitted on the wings; for D_2O it was simply drawn in as a straight line. For this region of Q the inelastic component is a very weak function of the temperature.

The shape of the distribution-in-energy of the quasi-elastic component is expected[2] to be approximately that of a Lorentz function $[W^2+(\hbar\omega)^2]^{-1}$, where W is the half-width at half maximum of the distribution. After correction for resolution[7] the spectra of Fig. 1 are consistent within the errors with Lorentz functions. On the approximation of small motions[2] (equivalent to Vineyard's Gaussian approximation[3]), the width $W=Q^2D_S$, where D_S is the coefficient of self diffusion for small motions. In Fig. 2 the measured values of W/Q^2 are compared with values of the coefficient of self diffusion of water, as measured using nuclear magnetic resonance by Simpson and Carr,[8] and using tracer methods by Graupner and Winter.[9] Other tracer measurements by Wang, Robinson, and Edelman[10] have given still larger values for D. Despite the large errors in the neutron measurements and disagreements in the self-diffusion measurements, it seems clear that the approximation of small motions[2,3] is not adequate and that a variety of diffusive motions must occur.

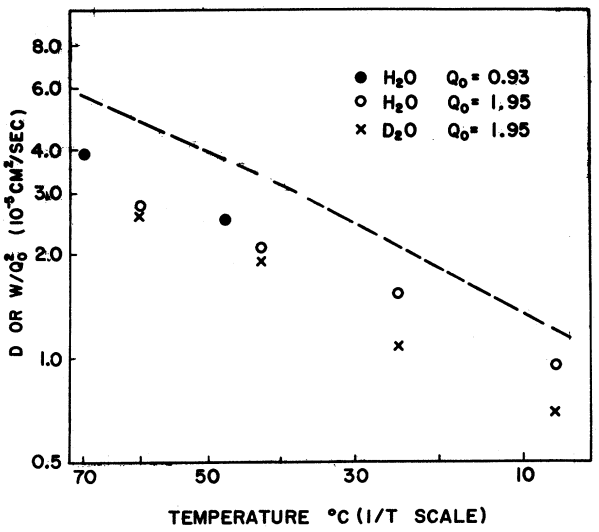

FIG. 2. Values of W/Q_0^2(log scale) plotted against the inverse temperature. The dashed line represents the nuclear magnetic resonance measurements of the diffusion coefficient by Simpson and Carr.

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[4] The inelastic component for D_2O was if anything narrower than that for H_2O at the position of the diffraction maximum of D_2O. The energy distributions of D_2O and H_2O were thus markedly different (by as much as 50%) even for quite small energy transfers, which are believed to arise from motion of the molecules as units. On the face of it this fact suggests the failure of Vineyard's convolution approximation for the pair correlation function (reference 3).

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[6] With the flight path of 4.5 meters and the repetition rate of 16 400 bursts/minute, the fastest neutrons inelastically scattered by light water arrived at the detector at the same time as the slower neutrons of the quasi-elastic group from the preceding burst. Approximate corrections were applied using the knowledge gained in the experiments of reference 2. For light water at $Q_0=1.95$ this involved comparatively large corrections between 4.2 and 5 A.

[7] The resolution function is approximately Gaussian. Tables of convolutions of the Lorentz function with a Gaussian resolution function were used to make the resolution corrections [V. L. Sailor, Brookhaven National Laboratory Report BNL-257 (unpublished); and Rose, Miranker, Leak, Rosenthal, and Hendrickson, Westinghouse Electric Corporation Atomic Powers Division Report WAPD-SR-506 (unpublished)].

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