# Quasielastic scattering of neutrons in water

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The spectrum of quasielastic neutrons in water has a complicated structure, due to rotations of the molecules. At momentum transfers $k < 2$ Å$^{-1}$, this spectrum is satisfactorily described by two components. It then becomes possible to extract information on the microdynamics and structure of water.

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The results of neutron experiments on water and on other molecular liquids[1,2] yield results that differ from the theoretical ones. The simplest dynamic models of a liquid[3] turn out to be too crude for the analysis of quasielastic scattering of neutrons. For example, it was observed that the quasielastic peak wings corresponding to large energy transfers decrease more slowly than called for by the theory.

In 1966, Ivanov proposed an approach to the problem of neutron scattering in liquids, an advantage of which is the possibility of taking into account all elements of molecular motion.[4] He has also taken additional account of random rotational-type reorientations of the molecules. In this case, the cross section for quasielastic scattering of the neutrons is described by a sum of Lorentz functions with different intensities and widths (see formula (19) of[4]). In par-

  

ticular, for momentum transfers $\kappa \lesssim 2$ Å$^{-1}$ ($\vec{\kappa} = \mathbf{k} - \mathbf{k}_0$), an analysis of the indicated formula yields a two-component form of the spectrum:

$$\frac{d^2\sigma}{d\epsilon\, d\Omega} = a^2 \frac{k}{2\pi\hbar k_0} \left( J_0(\kappa) \frac{\Gamma_0(\kappa)}{\Gamma_0^2(\kappa) + \epsilon^2} + J_1(\kappa) \frac{\Gamma_1(\kappa)}{\Gamma_1^2(\kappa) + \epsilon^2} \right). \tag{1}$$

Generally speaking, the form of the functions $\Gamma_m(\kappa)$ ($m = 0$ and 1) is complicated.

However, in regions of relatively large and relatively small $\kappa$, they take on rather simple forms.[1)]

At large $\kappa$ we have

$$\Gamma_m(\kappa) = \frac{\hbar}{\tau}(1 - \gamma A_m) + \hbar\kappa^2 D_1 - \frac{\hbar a(\kappa)}{T} f_m(\kappa),$$
$$\gamma = \frac{T}{T + T_1}, \quad \tau = \frac{TT_1}{T + T_1}, \quad A_m = e^{-2W} \cos m\chi, \tag{2}$$

where $T_1$ and $T$ are the lifetimes of the molecules relative to rotations and translational jumplike displacements, respectively; $D_1$ is the coefficient of continuous diffusion which characterizes the wandering of the molecules together with their surrounding; $\chi$ is the average angle of molecule rotation; $e^{-2W}$ is the Debye-Waller factor.

With respect to the functions $f_0$ and $f_1$ it is known that $f_0 \to 1$ and $f_1 \to 0$ as $\kappa \to 0$, and that $f_0 + f_1 \approx 1$ in the region $\kappa \sim 2$ Å$^{-1}$ (a plot of $f_m(\kappa)$ is shown in Fig. 1 of[5]).

The Fourier transform $\alpha(\kappa)$ of the distribution function of the lengths of the jumplike translational displacements decreases monotonically with increasing $\kappa$ and $\alpha(\kappa) \ll 1$ already at $\kappa \sim 2$ Å$^{-1}$.

In the region of small $\kappa$ we have

$$\Gamma_0(\kappa) = \hbar\kappa^2 D, \tag{3}$$

where $D$ is the coefficient of the total diffusion of the hydrogen atoms of the molecule, and $\Gamma_1(\kappa)$ tends as $\kappa \to 0$ to a constant value

$$\Gamma_1(\kappa) = \frac{\hbar}{\tau}(1 - \gamma \cos\chi).$$

In the region of intermediate $\kappa$ we have $\Gamma_1(\kappa) < \Gamma_1(0) + \hbar\kappa^2 D_1$.

In the analysis of our experimental data we could not describe satisfactorily the quasielastic peaks by a single Lorentz function (Fig. 1a), but these peaks are sufficiently well described by two functions (Fig. 1b).[2)]

Each of the components 1 and 2, is characterized by its own width $\Gamma_0$ and $\Gamma_1$, respectively. Their dependences on $\kappa^2$, represented in Fig. 2, reflect qualitatively the predictions of the theory. Indeed, in the region $\kappa^2 \approx 2$ Å$^{-2}$, the widths assume their asymptotic forms and $\Gamma_1(\kappa)$ tends to a finite value as $\kappa \to 0$. The difference between the slopes of $\Gamma_0$ and $\Gamma_1$ at large $\kappa^2$ seems to be due to the influence of the factor $e^{-2W}$.

| $D_1$, cm$^2$/sec | $T_1$, sec | $T$, sec | $\gamma$ | $\bar{\chi}$ |
|---|---|---|---|---|
| $(0.8 \pm 0.1) \times 10^{-6}$ | $2 \times 10^{-12}$ | $2.2 \times 10^{-10}$ | 0.96—0.98 | 60° |

Using the formulas given above, we can determine from Fig. 2 the microdynamic parameters of the water

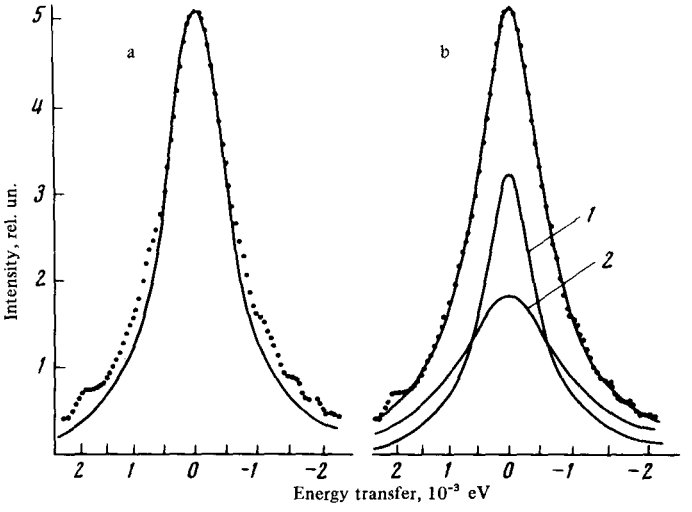


FIG. 1. Experimental points: a—Lorentz function with best fit to the experimental data; b—1,2—Lorentz function for $m=0$ and $m=1$, respectively; solid curve—resultant function describing best the experimental data.

We see that the jumplike displacements are relatively rare, the relative probability of reorientation is large, and consequently the role of rotational diffusion is likewise large. In other words, rotations change the diffusion coefficient that serves to describe the quasielastic scattering of neutrons in the region of small $\kappa$.

The large value of $T$ and the small value of the coefficient of continuous diffusion $D_1$, which describes the wandering of the groups of molecules, offer evidence that water is quasi-crystalline. Using the Stokes-Einstein formula $D_1 = KT/6\pi r\eta$, which connects the coefficient of translational diffusion $D_1$ with the viscosity $\eta$ and with dimension $r$ of the diffusing particle, we can estimate the dimensions of these groups. It turns out to be of the order of 60—70 Å. The possible existence of similar globules, with dimensions estimated at ~30 Å, is discussed in certain papers devoted to water.[6]

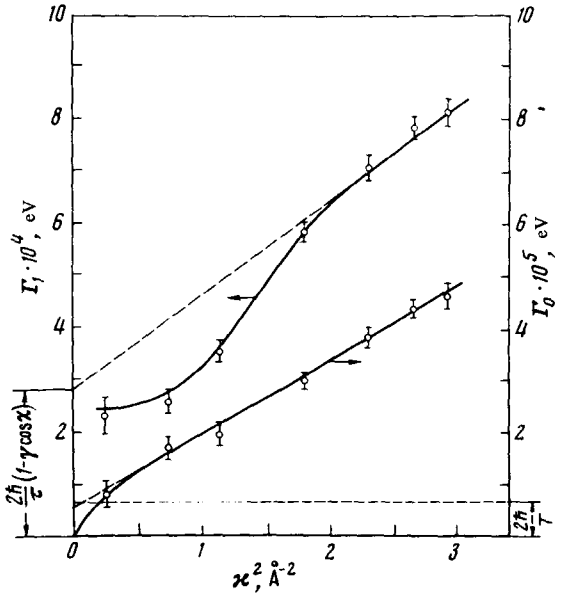


FIG. 2. Angular dependence of the component widths.

Thus, in addition to a satisfactory description of the experimental spectrum as a whole, the method developed by G. K. Ivanov turns out to be most informative not only with respect to the microdynamic characteristics of water, but also with respect to its structure. It can be added that when the experimental accuracy is increased it will be possible to determine also the molecule-range functions $\alpha(\kappa)$.

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[1)]These limiting cases were considered by G. K. Ivanov at our request.

[2)]The resolution of the experimental spectra into components was carried out by least squares with a computer, taking into account the resolution function of the crystal spectrometer, which is well approximated by a Gaussian function with $\Delta E/E \approx 0.04$. The sample thickness was 0.5 mm. The sample temperature was $t = 25\,^{\circ}C$.

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