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Proton Motions in Complex Hydrogenous Liquids. II. Results Gained from Some Neutron-Scattering Experiments

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In an accompanying paper, a cross section for the quasi-elastically scattered neutron spectra from certain types of hydrogenous liquids is given. In the present paper a comparison is made between this theoretical model and some neutron-scattering results obtained on *n*-propyl alcohol and pentane. The quasi-elastically scattered neutron intensity is analyzed in terms of the relaxation times τ_0, τ_1, τ_0', and τ_1', the jump length l of the proton, and the self-diffusion coefficient D of the molecular center of gravity. The nature of the quasi-elastically scattered neutron intensity is generally interpreted as a result of mixed protonic jumps and molecular diffusion. It is shown that the diffusion coefficients derived from neutron-scattering data consist of a combination $D+l^2/2\tau_0$, where for very low viscosities D dominates and for higher viscosities the protonic diffusion constant $l^2/2\tau_0$ dominates. Protonic jump lengths of 1.5 Å are observed. Definite values of the relaxation times τ_{00}, τ_0', and τ_0 are derived from the width of the quasi-elastic line. With the present resolution of the experimental equipment, times τ_{00} in the range 10^{-12} to 2×10^{-11} sec may be studied. It is shown how in the low-temperature, high-viscosity ranges, τ_0' is much larger than τ_0, the internal mean lifetime for a proton in a fixed-position. τ_0 values in a range from 10^{-11} to 2.5×10^{-12} are derived, whereas derived values of τ_0' for *n*-propyl alcohol range from 2.5×10^{-9} to 2.75×10^{-12} sec in a temperature range from 153 to 333°K. It is also shown for the case of pentane that when larger momentum transfers are studied in quasi-elastic scattering, the intensity of the resulting gaslike scattering picture is governed by a Debye-Waller factor. This is due to the fact that even if the center of gravity is moving like a gas particle, the proton jumps within the molecule continue. These results indicate that the quasi-elastic scattering has two components: a diffusive component of width $2\hbar(D+l^2/2\tau_0)\kappa^2$ and a gas component the width of which depends upon the degree of hindrance for the free recoil of a molecule in a collision. Which component dominates depends upon the magnitude of the momentum transfer $\hbar\kappa$ in the scattering process.

1. MODEL CONSIDERATION

In Paper I of this work a theory was given for the neutron-scattering cross section of protons in a liquid consisting of complex molecules. It was assumed that two types of motions occur, namely:

(a) Motions of the center of gravity hindered by various kinds of forces such as those created in a hydrogen bond. Hindrances to the molecular motions also exist in other liquids, such as the van der Waals liquids. The molecule is supposed to move in distinct phases of motion characterized by a vibrational period τ_0' and a diffusive period τ_1'. The vibration gives rise to a Debye-Waller factor $2W_e=\frac{1}{6}\langle r_e^2\rangle\kappa^2$, which is small because of the large masses of the molecules considered. The diffusive period gives rise to an unobservable diffusion constant D_e such that $D=D_e\tau_1'/(\tau_1'+\tau_0')$, where D is the true macroscopic diffusion constant.

(b) Motions of the proton within the molecule (or possibly a proton jump between molecules). This motion is thought of as a hindered rotation consisting of a vibration assumed to exist for a time τ_0, followed by a rapid jump performed in a very short time τ_1.

The vibrational period gives rise to a Debye-Waller factor, which, however, in this case is supposed to have two contributions: $2W_i=(2W_i)_t+(2W_i)_r$, where the first part is a translational contribution of the conventional form:

$$(2W_i)_t=\frac{\hbar^2\kappa^2}{2M}\int_0^\infty \coth\frac{\hbar\omega}{2k_BT}f(\omega)\frac{d\omega}{\omega}=u_t^2\kappa^2 \tag{1a}$$

and the second part originates from the torsional oscillations[1]:

$$(2W_i)_r=\frac{\hbar^2\kappa^2}{2M_rE_r}\coth\frac{E_r}{2k_BT}=u_r^2\kappa^2. \tag{1b}$$

Here M is the molecular mass, M_r is the effective rotational mass of the molecule, $f(\omega)$ is the frequency distribution of the hindered translational motions, and E_r is the energy of the torsional oscillation. The hindered rotational motion of the proton is considered as an isotropic, harmonic, and monoenergetic oscillation such that $f(\omega)$ in Eq. (1a) is replaced by $\delta(\hbar\omega-E_r)$ to obtain (1b). (Compare Ref. 1, p. 124.)

The short jump period during which the proton moves with an average speed v is characterized by the jump length $l=v\tau_1$.

The theory thus contains several parameters, and it might be argued that any fit to the observed data using this theory with the parameters τ_0', τ_1', τ_0, τ_1, D, l, and W_i is quite arbitrary. It will, however, be seen that several of these parameters are determined separately from the neutron-scattering data. For small and medium transfers, $0<\kappa<3$ Å^{-1}, in the scattering process, it is always found that the neutron-scattering picture con-

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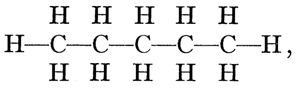
[1] T. Springer, Nukleonik 3, 110 (1961).

sists of two parts, a broad inelastic spectrum and a rather narrow quasi-elastic peak. In this work we will deal almost exclusively with the quasi-elastic peak, the intensity distribution of which was discussed in Paper I. It is anticipated that a separation of the quasi-elastic peak from the inelastic background is allowed and has a clear physical meaning in the complex hydrogenous liquids considered here.

2. MEASUREMENTS

At the Stockholm reactor R1 studies of slow-neutron scattering from a series of hydrogeneous liquids over a wide range of temperatures have been performed. In this work we shall deal only with two of these liquids, namely,

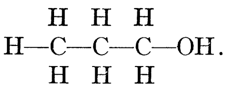
pentane:



$$\begin{array}{ccccccccccccc} & & H & & H & & H & & H & & H & & \\ H & - & C & - & C & - & C & - & C & - & C & - & H, \\ & & H & & H & & H & & H & & H & & \end{array}$$

and

n-propyl alcohol



$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ H & - & C & - & C & - & C & - & OH. \\ & & H & & H & & H & & \end{array}$$

These two liquids form an interesting pair. The *first* one is a van der Waals liquid without any hydrogen bonds, being characterized by the C-C bonds round which torsional oscillations and partial, isomeric rotations of CH_3 and CH_2 groups are possible. The *second* liquid partly shows C-C bonds like pentane, but the carbon chain is ended by one hydrogen bond which prohibits the rotation of the whole molecule. In propyl alcohol one should thus expect both internal proton jumps and molecular motions of a type determined by the temperature of the sample. Pentane corresponds to a situation with a minimum of hindrances against isomeric rotations and also against diffusive motions.

Pentane was studied in a temperature range from 238 to 293°K and *n*-propyl alcohol in a range from 153 to 333°K. In all cases the beryllium-filtered cold-neutron spectrum was sent into the samples of thickness of about 0.2 mm showing a transmission to 4-Å neutrons of approximately 90%. In some cases a higher neutron energy was selected from the reactor spectrum using the Stockholm crystal spectrometer[2] and a Bucharest crystal spectrometer.[3] Thus the studies of the quasi-elastic peak obtained from pentane at 293°K were made using both types of ingoing neutron spectra. In Stockholm the slow-chopper time-of-flight technique was used for the energy analysis of the scattered spectra, whereas at Bucharest a second crystal served this purpose. A large number of scattering angles between 11° and 130° were used to cover a wide range of κ values such that $0.3\ \text{Å}^{-2} < \kappa^2 < 6\ \text{Å}^{-2}$.

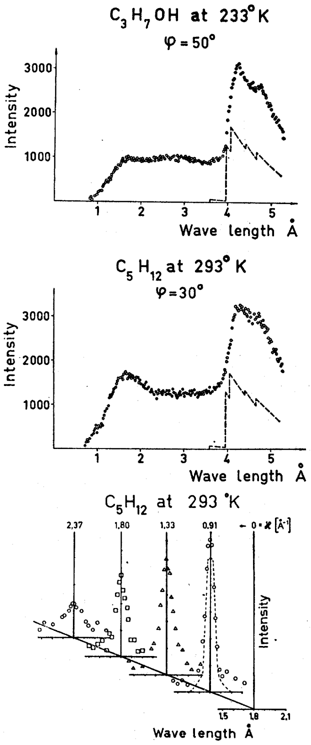


FIG. 1. Examples of observed neutron spectra scattered from various hydrogenous samples using cold neutrons at the Stockholm reactor and thermal neutrons at the Bucharest reactor. Ingoing spectrum shape is given by dashed lines.

Typical examples of observed scattered-neutron spectra using different ingoing-neutron spectra are given in Fig. 1. As has been discussed[4] in great detail earlier, the natural width of the quasi-elastic peak was obtained from the observed broadening of the ingoing spectrum by comparison of the observed quasi-elastic peak with a calculated one obtained by folding a Lorenz function with a Gaussian resolution function of known width and then folding this combined function with the ingoing spectrum shape. The resolution $\delta t/t$ of the analyzer part of the spectrometer at 4 Å was 2%. The resolution $\delta\lambda/\lambda$ of the monochromator part when using the crystal–time-of-flight spectrometer was 4%. Natural linewidths in a range $3\times10^{-5} < \Delta E < 1\times10^{-3}$ eV could be extracted from the observed data using the cold-neutron technique. The smallest values of ΔE were obtained from *n*-propyl alcohol at the lowest temperatures used. Width values smaller than these cannot be obtained unless much longer neutron wavelengths are used or unless the resolution is increased. When the full cold-neutron spectrum is used, larger width values than those corresponding to $\Delta E \simeq 1$ meV cannot be analyzed, because then any separation of the quasi-elastic peak from the inelastic background becomes impossible. Only with high-flux reactors may the present observations be extended to smaller κ values and the precision be increased over the ranges of medium and small κ values. If higher ingoing-neutron energies are used, large κ values and consequently large line broadenings are easily produced. The final result of the

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[2] U. Dahlborg, K. Sköld, and K. E. Larsson, in *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1965), p. 487.

[3] S. Ripeanu, Rev. Roum. Phys. (to be published).

[4] K. E. Larsson and U. Dahlborg, Physica **30**, 1561 (1964).

TABLE I. Data for *n*-propyl alcohol.

T (°C)	η (poise)	$u_t^2+u_r^2$ (Å^2)	τ_{00} (10^{-12} sec)	τ_0' (10^{-12} sec)	τ_0 (10^{-12} sec)	"D" (10^{-5} cm^2/sec)	D (10^{-5} cm^2/sec)	l^2 (Å^2)
−120	55	0.069	13.5	2500	13.2	1.0	···	2.70
−100	6.4	0.10	8.5	580	9.6	1.3	···	2.21
−55	0.22	0.13	5.4	54	5.6	1.8	0.04	2.10
−40	0.13	0.14	4.3	29	4.9	2.2	0.08	2.12
−10	0.052	0.15	2.95	11.2	3.95	3.5	0.24	2.67
+20	0.022	0.19	1.95	5.0	3.3	4.0	0.58	2.27
+50	0.011	···	1.45	2.75	2.9	5.0	1.1	2.32
							Mean value	2.34

analysis of the quasi-elastic peak is the full width at half-maximum ΔE given as a function of the square of the momentum transfer κ^2 or in some cases as a function of κ.

A parameter of importance for the interpretation for the data is the Debye-Waller factor $2W_i$ for the proton motion relative to the molecular center of gravity. As was seen in Paper I, the integrated cross section $d\sigma/d\Omega$ is governed by the well-known factor $\exp(-2W_i)$. If the logarithm of the observed intensity is plotted versus κ^2, one automatically obtains the sum $u_t^2+u_r^2$ according to Eqs. (1a) and (1b). If the beryllium-filled cold-neutron spectrum is used for the investigation, the intensity is determined by the intensity at half-maximum multiplied by the width value uncorrected for resolution.[5] If the ingoing spectrum is shaped by a crystal spectrometer, the full area of the separated quasi-elastic peak defines the intensity to use in the determination of $u_t^2+u_r^2$.

3. RESULTS

A. *n*-Propyl Alcohol

As shown by Fig. 2, all the linewidth data reveal the same tendency: For larger κ values the linewidths tend toward a constant value. This is a behavior described by cases I and II of our theory, which both correspond to a bonding situation such that $\tau_1'\ll\tau_0'$. The limiting value of the linewidth for larger κ values is $2\hbar/\tau_{00}$, where $\tau_{00}\simeq\tau_0$ in case I ($\tau_0'\gg\tau_0$), and $\tau_{00}^{-1}=\tau_0^{-1}+\tau_0'^{-1}$ in case II (τ_0' is of the same order as τ_0). In the case of propyl-alcohol τ_0' is to be identified with the mean lifetime of the hydrogen bond, whereas τ_0 is the mean time between two successive rotational jumps of a CH_3—, a $CH_3\cdot CH_2$—, or a $CH_3\cdot CH_2\cdot CH_2$— group within the molecule. As the viscosity[6] of *n*-propyl alcohol is high at our four lowest temperatures −120°C, −100°C, −55°C, and −40°C (compare Table I) we fit our linewidth formula

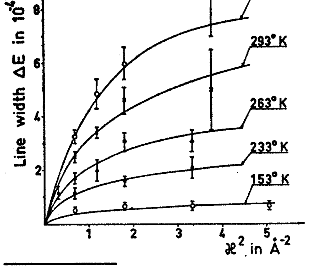

FIG. 2. Observed widths of quasi-elastic lines obtained from cold-neutron scattering on *n*-propyl alcohol. The solid lines correspond to the best fit of the theoretical widths given in Paper I to the observed data.

$$\Delta E=\frac{2\hbar}{\tau_{00}}\left(1-\frac{\rho_A}{\tau_1}e^{-2W_i}\right) \tag{2a}$$

to the data at these temperatures. At the next three temperatures −10, +20, and +55°C, the viscosity is moderate and we use our case-II formula to fit to the data;

$$\Delta E=\frac{2\hbar}{\tau_{00}}\left(1-\frac{\tau_{00}}{\tau_0}\frac{\rho_A}{\tau_1}e^{-2W_i}-\frac{(\tau_{00}/\tau_0')e^{-4W_i}}{1+D_e\kappa^2\tau_1'}\right). \tag{2b}$$

It is seen that in both cases a value is needed for the Debye-Waller factor $2W_i$. This was experimentally determined as discussed above, and the values of $u_t^2+u_r^2$ are given in Table I. Furthermore, the integral ρ_A/τ_1 is dependent on the value of the jump length $l=v\tau_1$. As discussed in Paper I, the slope at the origin of the linewidth curves is given by

$$(2\hbar/\tau_0)\left(\tfrac{1}{2}l^2+\tfrac{1}{6}\langle r_i^2\rangle\right)=2\hbar\text{"}D\text{" in case I} \tag{3a}$$

and by

$$(2\hbar/\tau_0)\left[\tfrac{1}{2}l^2+\tfrac{1}{6}\langle r_i^2\rangle(1+2\tau_0/\tau_0')+D\tau_0\right] =2\hbar\text{"}D\text{" in case II}. \tag{3b}$$

As a first approximation a curve is drawn by free hand through the experimental points and the "D" value is determined. It is immediately seen that "D" is much larger than the values of $\frac{1}{6}\langle r_i^2\rangle/\tau_0$ given in Table I. Therefore "D"$\simeq l^2/2\tau_0$, at least at the lowest temperatures, where τ_{00} is expected to be practically identical with τ_0 and the true self-diffusion constant D is very small.

From the lowest temperature observations a value of $l=(2\text{"}D\text{"}\tau_0)^{1/2}=1.5$ Å is obtained, and as l is expected to be rather independent of temperature, this l value is

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[5] K. E. Larsson, S. Holmryd, and K. Otnes, in *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1961), p. 329.

[6] T. Lyon and T. A. Litowitz, J. Appl. Phys. **27**, 179 (1956).

—as a first approximation—used throughout at all temperatures. A first approximate value of τ_0 is simply obtained from the limiting value of the linewidth at larger κ values. Having this approximate l value, the full linewidth curves may be calculated because ρ_A/τ_1 as well as $2W_i$ is known. The only important adjustable parameter left is the limiting linewidth value τ_{00}, which is to be determined. τ_{00} is now found by a fit of either of the two linewidth formulas given above to the experimental data. The resulting values are given in Table I and Fig. 3. Examples of the type of fit to the observed linewidth data that are obtained using our formulas (2a) and (2b) are given in Fig. 2. In order to use formula (2b) a value of $D \simeq D_e(\tau_1'/\tau_0')$ is needed. Measurements of the self-diffusion coefficient for *n*-propyl alcohol have been performed by Partington *et al.*[7] and we used their values and extrapolations thereof assuming $D = 7.7 \times 10^{-3} e^{-2100/T}$ in our temperature interval. Furthermore, in using Eq. (2b) something has to be assumed about the division of τ_{00} into τ_0 and τ_0'. Since in the beginning nothing is known about this, one may start by assuming $\tau_0 = \tau_0'$ for the three highest temperatures. This seems rather arbitrary but as is seen from Fig. 2 of Paper I of this work, the difference between the calculated line shapes for the cases I and II, corresponding to $\tau_0' \gg \tau_0$ and $\tau_0' = \tau_0$, respectively, is fairly small.

Returning to Fig. 3, which gives the derived values of τ_{00} as a function of temperature, one finds that the outstanding feature of the data is a marked faster decrease of τ_{00} at higher temperatures. Also the observations at the four lowest temperatures, for which the viscosity is high, are seen to fall practically on a straight line, suggesting that at these low temperatures $\tau_{00} \sim e^{a/T}$. Furthermore—as is seen from Fig. 4—the derived apparent diffusion constant "D" is orders of magnitude larger than the self-diffusion constant observed by Partington *et al.* This indicates that at these low temperatures the neutron observes only the isomeric, jump-like rotations of the protons within the molecule. Therefore the conclusion is drawn that at these low temperatures $\tau_0 \sim \tau_{00} \sim {}^{a_1/T}$. At the other temperature end of the curve the slope is seen to increase sharply, which suggests that τ_0' dominates more at higher temperatures, which means that here $\tau_0' < \tau_0$ and consequently the mean lifetime of a hydrogen bond is shorter than the mean time between rotational jumps within the molecule. If we assume $\tau_0' \sim e^{a_2/T}$, we find that τ_{00} must be represented in the following way:

$$\frac{1}{\tau_{00}} = \frac{1}{\tau_0} + \frac{1}{\tau_0'} = c_1 e^{-a_1/T} + c_2 e^{-a_2/T}. \tag{4a}$$

Here a_1 and a_2 play the role of activation energies. A very good fit to the data (compare Fig. 3) is obtained

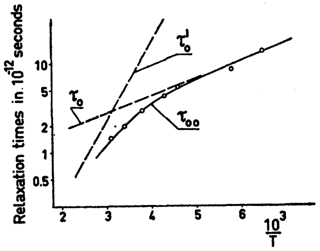

FIG. 3. Relaxation times for protonic motions in *n*-propyl alcohol derived from linewidth data.

with

$$\frac{1}{\tau_{00}} = 1.4 \times 10^{12} e^{-450/T} + 1.8 \times 10^{14} e^{-20000/T}. \tag{4b}$$

The activation energy for τ_0 is thus 450°K or 0.9 kcal/mole and the activation energy for τ_0' is 2000°K or 4 kcal/mole. It is important to note that the value of 0.9 kcal/mole is in good agreement with the values of activation energies of isomeric rotations in carbon chains like those in pentane observed by infrared technique. The value of 4 kcal/mole should be the activation energy for the hydrogen bond in *n*-propyl alcohol. This ought to be identical with the activation energy for self-diffusion. From the data of Partington *et al.* one finds a value of 4.2 kcal/mole, in very gratifying agreement with our derived value of 4.0 kcal/mole.

Returning again to the slope at the origin of our linewidth data giving the apparent diffusion constant "D", the observed data are given in Fig. 4. Having now more accurate data for τ_0 and τ_0' it is possible to calculate l^2 more accurately from Eqs. (3a) and (3b). In general one finds $\frac{1}{3}\langle r_i^2 \rangle \ll l^2$ and therefore Eqs. (3a) and (3b) may be approximated by $(2h/\tau_0)(\frac{1}{2}l^2 + D\tau_0)$, so that

$$l^2 = (\text{“}D\text{”} - D) 2\tau_0 = 2\tau_{00}(1 + \tau_0/\tau_0')(\text{“}D\text{”} - D). \tag{5}$$

Using this formula, l^2 is calculated for each temperature using our measured values τ_{00}, τ_0, τ_0', and "D" combined with Partington's values for D. The result is seen in the last column of Table I. It is clear that l^2 comes out as a constant, independent of temperature within about 5%. The mean value of l^2 is 2.34 Å^2, corresponding to $l = 1.53$ Å.

This analysis was started by assuming approximately $l = 1.5$ Å and $\tau_0' = \tau_0$. It is again repeated using the first obtained experimental values and a rapid convergence in this iteration procedure is found. The values of τ_0', τ_0, "D", and l given here in Table I and in the figures

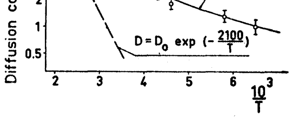

FIG. 4. Apparent protonic diffusion coefficient for *n*-propyl alcohol derived from the neutron-scattering data compared with the true molecular self-diffusion coefficient.

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[7] J. R. Partington, R. F. Hudson, and K. W. Bagnall, J. Chem. Phys. **55**, 77 (1958).

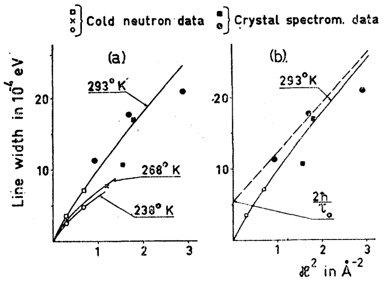

FIG. 5. (a) Observed linewidths in pentane using cold and thermal neutrons. Observations performed in Stockholm and Bucharest. (b) Comparison between observed linewidth data and the expected theoretical width for room-temperature pentane.

are the final results of this procedure. If now "D" is calculated using (5), i.e., "D"$=D+l^2/2\tau_0$, one finds an excellent agreement with our observed "D" values (compare Fig. 4).

To sum up, the linewidth data obtained on n-propyl alcohol may be fully understood on the basis of our theory. The parameters derived form a consistent set. It is interesting to note that the constant giving the numerical value of $1/\tau_0$ is 1.4×10^{12}. If it is assumed that

$$\frac{1}{\tau_0}=\frac{\omega}{2\pi}e^{-E/k_BT}, \tag{6}$$

where $\omega/2\pi$ is the frequency of the torsional oscillation of the CH_3—, $CH_3\cdot CH_2$—, or $CH_3\cdot CH_2\cdot CH_2$— groups, it is seen that this frequency should be 1.4×10^{12} sec^{-1}. In the generalized frequency distributions derived from the inelastically-scattered-neutron spectra from several hydrogenous liquids[4] the molecules of which consists of a chain of CH_2 groups, a peak seems to occur at just this frequency $\omega\sim10^{13}$ sec^{-1}. This peak may be a spurious one but it is quite interesting to note the coincidence. The use of a narrower ingoing-cold-neutron spectrum will solve this problem.

B. Pentane

i. $\kappa^2<3$ *Å*$^{-2}$

The pentane molecule is not hindered in its motion by any hydrogen bond. Nevertheless, in the liquid state it is not free to move as in a gas. This is clearly shown, not only for pentane but for various kinds of fluids, by the important role played by the free volume in the viscosity of liquids.[8] It is found that macroscopically the observed viscosity is best described by a formula which combines the effect of the free volume available for a molecule to jump into, and the activation energy to overcome the barrier and make the jump into another site. If the molecule as a whole is hindered in its motions, then internal motions like stepwise rotations may occur, as we saw in the previous example. Even if the hindrance for the molecular motions disappears, the internal rotations will continue, the necessary energy being supplied by collisions. As was shown in Paper I, the nature of the quasi-elastically scattered neutron intensity will be quite different from what was observed for the propyl alcohol case if the hindrances for self-diffusion are small, i.e., if $\tau_1'\gg\tau_0'$. As soon as τ_1' becomes larger than τ_0' the limiting behavior of the linewidth for larger κ values will be that typical for simple diffusion. If, however, τ_0 is not infinite (there are no internal rotations if $\tau_0\rightarrow\infty$), the diffusive behavior is reached asymptotically and the asymptote cuts the ΔE axis at $2\hbar/\tau_0$. This corresponds to cases III and IV of our theory in Paper I.

In the temperature range, $-35°\text{C}<T<+20°\text{C}$, within which we investigated our pentane sample, its viscosity is very low: $0.43\text{ cP}>\eta>0.23\text{ cP}$. These values are at least one order of magnitude lower than those for which we investigated propyl alcohol. It is therefore to be expected that molecular diffusive effects will show up. This is indeed in line with our width observations on pentane, which show that the broadening of the quasi-elastic peak is so much larger than for propyl alcohol, that only for κ values <1 Å^{-1} could linewidths be analyzed using cold neutrons [Fig. 5(a)]. To obtain width values at somewhat larger κ values the crystal monochromator was used. The accuracy is good enough to show that there is no tendency toward linewidth saturation as in propyl alcohol for κ values <3 Å^{-2}. The behavior of the observed linewidth values for $\kappa^2>3$ Å^{-2} will be treated separately below. Concentrating only on the observations for $\kappa^2<3$ Å^{-2}, one may conclude that diffusive behavior is asymptotically reached. This means that in the analysis along our theoretical lines we apply the cases III or IV.

We assume $\tau_1'\gg\tau_0\gg\tau_0'$. Under these assumptions our theory predicts a linewidth

$$\Delta E=\frac{2\hbar}{\tau_0}\left(1+D\kappa^2\tau_0-\frac{\rho_B}{\tau_1}e^{-(\langle r_i^2\rangle/6)\kappa^2}\right). \tag{7a}$$

When κ increases towards large values one finds

$$(\Delta E)_{\kappa\to\infty}=2\hbar[1/\tau_0+D\kappa^2]. \tag{7b}$$

The slope at the origin is given by

$$(\Delta E)_{\kappa\to0}=2\hbar(D+l^2/2\tau_0+\langle r_i^2\rangle/6\tau_0)\kappa^2. \tag{7c}$$

The last formula means that if $l^2\gg\frac{1}{3}\langle r_i^2\rangle$, then the apparent diffusion constant derived from the slope at the origin is

$$\text{"}D\text{"}=D+l^2/2\tau_0. \tag{8}$$

This is identical with the results (3a) and (3b), for n-propyl alcohol, if appropriate approximations are made. The value of "D" is easily derived from the data in Fig. 5(a). A measurement of the self-diffusion coefficient D at $T=293°\text{K}$ was made by McCall *et al.*,[9] and these authors also give an activation energy of 1.6 kcal/mole. If these data are used, a value of l^2/τ_0 may be found using Eq. (8). As the same type of carbon chain exists in n-propyl alcohol and in pentane, we assume $l^2=2.34$ Å^2 for pentane. This gives a solution of

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[8] P. B. Macedo and T. A. Litowitz, J. Chem. Phys. **43**, 245 (1965).

[9] D. W. McCall, D. C. Douglas, and E. W. Anderson, Phys. Fluids **2**, 87 (1959).

TABLE II. Data for pentane.

T (°C)	η (poise)	D (10^{-5} cm²/sec)	"D" (10^{-5} cm²/sec)	τ_0 (10^{-12} sec)
−35	0.0043	2.79	6.5	3.2
−5	0.0030	4.05	8.4	2.7
+20	0.0023	5.25	10	2.5

τ_0 and makes it possible to construct the asymptote which the linewidth curve approaches for larger values of κ [compare Fig. 5(b)]. All the derived data for the observations on pentane are given in Table II.

In order to calculate the linewidth, using Eq. (7a), a value of the Debye-Waller factor $2W_i$ must be known. Using the technique described above we found $\frac{1}{6}\langle r_i^2\rangle = 0.28$ Å^2 for pentane at 293°K. With this value given as well as τ_0, D, and the value of ρ_B/τ_1 obtained from Fig. 1 of Paper I of this work, we calculate ΔE. As seen in Fig. 5(b), the agreement between the calculated linewidth curve and the observed data is reasonable up to a value of about 3 Å^{-2} for κ^2, and the calculated asymptote determined by τ_0 and D fits the observed behavior of linewidths.

If the liquid consists of molecules in which no proton jumps occur, as for instance in liquid methane CH$_4$, then $\tau_0 = \infty$ and our theory would predict a simple diffusive behavior if $\tau_1' \gg \tau_0'$. This has indeed been observed by Dasannacharya *et al.*,[10] who used a narrow cold-neutron spectrum to send into their liquid sample. It is interesting to notice that if a Debye-Waller factor is derived from their data, it will be of the order $2W_i = 0.55\kappa^2$. Comparing this Debye-Waller factor with the presently obtained ones, $\simeq 0.20\kappa^2$ for room-temperature *n*-propyl alcohol and $\simeq 0.28\kappa^2$ for room-temperature pentane, one tendency is obvious: the smaller the hindrance for rotation, the larger is $2W_i$. Considering (1a) and (1b), this is quite clear, the explanation being that the smaller the hindrance to rotation is, the smaller E_r in (1b) is also, and the larger consequently is the contribution of the torsional part to the Debye-Waller factor, $(u_t^2 + u_r^2)\kappa^2$. In liquid methane the hindrance to molecular rotation is rather small, and therefore E_r is small and u_r^2 is large, giving a large Debye-Waller factor. One might imagine that the thermal cloud of the proton is ellipsoidal, so that two degrees of freedom, the torsional oscillations, are associated with a larger mean-square deviation $u_r^2 = \frac{1}{4}\langle r_r^2\rangle$, and the third one is associated with a smaller mean-square deviation $u_t^2 = \frac{1}{2}\langle r_t^2\rangle$.

ii. $\kappa^2 > 3$ *Å*$^{-2}$

For larger momentum transfers, when κ^2 exceeds a value of about 3 Å^{-2}, a marked deviation occurs. This may be understood, if we remember that in deriving the cross-section formulas above it was assumed that the width function $\rho_{he}(t) = Dt$ for the unbound phase of the motion of the molecular center of mass. This is approximately correct for longer observation times $t \gg t_B$, where $t_B = M'D/k_BT$ is a delay time for the onset of diffusion. M' is an apparent effective mass of the molecule, larger than its real mass M. As shown by Schofield[11] one should, for smaller observation times corresponding to larger κ values, expect a width given by $(D/\tau_B)t^2$, which results in a quasi-elastic line of Gaussian shape with a full width at half-maximum given by

$$\Delta E = 2\hbar(2\ln 2)^{1/2}(D/\tau_B)^{1/2}\kappa. \qquad (9)$$

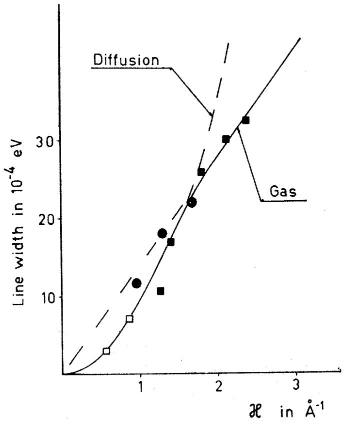

FIG. 6. Observed linewidths in pentane given as a function of κ. For $\kappa > \sqrt{3}$ Å^{-1} the momentum transfer is large enough to cause a gas-model scattering.

If the linewidth data of Fig. 5(b) are plotted on a linear κ scale and data for $\kappa^2 > 3$ Å^{-2} are added, as is done in Fig. 6, it is seen that there is a linear variation of ΔE versus κ for κ values $> \sqrt{3}$ Å^{-1}. For κ values $< \sqrt{3}$ Å^{-1} there is a parabolic variation of ΔE with κ as predicted by our formulas (7a), (7b), (7c). From the slope of the line in Fig. 6 a value of τ_B of 6.7×10^{-13} sec is derived. This is to be compared with the value of the corresponding Langevin delay time $t_\beta = MD/k_BT$, which is 1.6×10^{-13} sec. The mass ratio M'/M is thus $= \tau_B/t_\beta = 4$, indicating a relatively strong hindrance to diffusion of the pentane molecule. An inspection of Fig. 6 also tells how delicate the linewidth analysis may be, since the deviation from the straight line for $\kappa < \sqrt{3}$ Å^{-1} is large only for the smallest κ values. This means that only lone-wavelength neutrons should be used to study the finer details of quasi-elastic line shapes, if reasonably large angles of observations are to be used for a case like pentane.

Another very interesting fact associated with the observations of the "quasi-elastic" line for $\kappa > \sqrt{3}$ Å^{-1} is that if the logarithm of the area I of the peak is plotted versus κ^2 one does not obtain a constant and κ-independent intensity as predicted by the gas model. Rather, as seen in Fig. 7, the slope of the line indicates a Debye-Waller factor $u^2 = 0.25$ Å in excellent agreement with a value 0.28 Å obtained from observations at $\kappa < \sqrt{3}$ Å^{-1}. This is easily understandable, as the Schofield model

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[10] B. A. Dasannacharya, G. Venkataraman, and K. Usha Deniz, in *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1965), p. 157.

[11] P. Schofield, in *Fluctuation, Relaxation and Resonance in Magnetic Systems*, edited by D. ter Haar (Plenum Press, Inc., New York, 1963), p. 207.

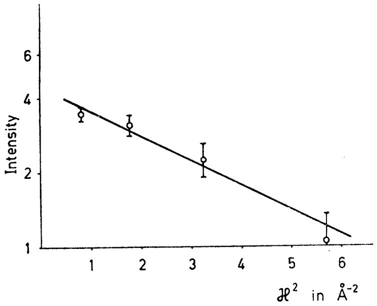

FIG. 7. Intensity of the quasi-elastic peak (for pentane at 293°K) plotted as a function of κ^2, showing that even for κ values $>\sqrt{3}$ Å^{-1} a Debye-Waller factor for the internal proton motions governs this peak intensity.

cited above deals only with the motion of the center of gravity. Even if the molecule moves freely as in a gas, internal proton jumps and vibrations will of course occur. Thus a Debye-Waller factor $2W_i$ must govern the quasi-elastic peak intensity even if this peak is described by the gas model for the motion of the center of gravity.

4. CONCLUDING REMARKS

Applying the theory which connects the dynamical phenomena in complex hydrogenous liquids with the quasi-elastic slow-neutron scattering curve, a consistent and natural explanation for the neutron-scattering observations may be derived. As the theory is phenomenological, it remains to caiculate the various relaxation times and other constants starting from first principles. Possible quantum-mechanical derivations of the relaxation times for molecular reorientations in solids have been devised. It could thus be possible that energy exchange between phonons or quasiphonons and protons in the rotational energy levels take place in the liquids considered here and is the fundamental cause for the relaxation mechanism. Such an explanation seems quite possible now that the existence of quasiphonons in liquids has been demonstrated experimentally.

It should also be pointed out that the theory of Paper I anticipates the existence of a single relaxation time for each process discussed. Should there happen to be a distribution of relaxation times, changes in the theoretical cross-section forms might occur. The various τ values discussed in these two papers should be considered as appropriate average values.

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Quantized Vortices in an Imperfect Bose Gas and the Breakdown of Superfluidity in Liquid Helium II*

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The energy and momentum associated with vortex formation in an imperfect Bose gas have been computed quantum mechanically. In the computation, explicit account is taken of the boundary condition to be satisfied by the wave function at the walls surrounding the fluid. Numerical estimates of the critical velocity obtained thereby throw considerable light on the question of the most favorable location (relative to the walls) for the formation of the vortex. It is concluded that the optimum location for this formation could be well within the fluid—significantly away from the walls.

I. INTRODUCTION

THE existence of quantized vortex rings as a mode of excitation in liquid helium II and their relevance to the phenomenon of breakdown of superfluidity are by now well established.[1-5] Accordingly, a number of attempts have been made in recent years to investigate the dynamics of these vortices and to obtain thereby theoretical estimates for the critical velocity of superflow.[6-9] The results so obtained are in general reasonable; nevertheless, a number of questions still

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