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Rotational and Translational Diffusion in Complex Liquids

K. E. Larsson
*Royal Institute of Technology, Stockholm, Sweden**

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In two earlier papers, a theoretical and experimental study of the dynamics of molecules in liquids or solids by the neutron-scattering technique was reported. Special attention was given to the quasi-elastically scattered neutron line, the shape and width of which contains considerable information regarding the details of the diffusive process, its origin and nature. It was shown that the origin and formation of the quasi-elastic peak may be understood if the molecular motion is divided into two partial motions: (1) the motion of the center of gravity, which might be diffusive or vibratory; (2) the motion relative to the center of gravity performed by the molecular constituents, of which the protons are the most important for the case of neutron scattering (this relative motion may be of rotational, hindered rotational, or vibrational nature). In the present work the basic ideas developed in the earlier papers are evolved further. A model for the relative motion of the molecule is defined, and a neutron cross section based on this model is worked out and applied to the neutron-scattering results on glycerol and *n*-propanol. It is assumed that the molecule performs a partially hindered rotation around an effective center of gravity so that each proton may be visualized as performing a vibrational motion around a center which is diffusing on the surface of a sphere. The diffusive motion might occur in small steps or in large jumplike steps. The resulting cross section for quasi-elastic scattering may approximately be described as a Lorentzian line with a full width at half-maximum that is a function of various parameters, such as the true self-diffusion coefficient $D_{\text{c.g.}}$, describing the motion of the molecular center of gravity, and a relative diffusion coefficient D_{rel}, describing the proton motion on the surface of the sphere. The relative diffusion coefficient has three components: one each due to small and to large displacements of the protons, corresponding to small and large changes of the molecular orientational angles, respectively; and one due to vibration. It is possible to fit the calculated widths to the observed ones over the entire temperature range investigated for the two liquids, and for the momentum ranges covered in the present studies. This leads to numerical values for the various parameters entering the theory. The values obtained for the various mean lifetimes for the motions are compared with relaxation times obtained from dielectric and ultrasonic data, and certain connections are established. The neutron experiments indicate that the true molecular diffusive motion is a mixed translational-rotational-vibrational displacement. The present work is limited to a study of such systems (complex liquids of not too low viscosity, or solids) in which the rotations are more or less strongly hindered. The consequence of the various neutron observations and other evidences is that the velocity autocorrelation for translational as well as rotational motion is strongly nonexponential for shorter times. The consequences of this for the interpretation of nuclear-magnetic-resonance, dielectric, and ultrasonic data are discussed.

I. INTRODUCTION

THE problem of interpretation of the spectra of slow neutrons scattered from liquids has been the subject of several recent studies both for simple[1–5] and for complex liquids.[1,2,6,7] In the present investigation cold neutrons from the Stockholm reactor were used to study in particular the quasi-elastic scattering from complex hydrogenous liquids.

In a recent development[8] of a statistical model for the motion of molecules in a liquid or solid surrounding, certain cross-section formulas were given for the quasi-elastic scattering of slow neutrons against such a system. It was explicitly shown that proton motion with respect to the molecular center of gravity leads to an observable and in some cases dominating broadening of the ingoing neutron line. The physical model for the molecular motion was as follows:

During the average time τ_0 the protons vibrate with respect to the molecular center of gravity. At the end of this period the proton jumps a certain distance l during a short time τ_1. The origin of these jumps was not clearly proposed in the previous paper. These vibrational and jumping periods were supposed to occur repeatedly. However, in the liquid phase after a certain time τ_0', it was assumed that the configuration around the selected molecule changes profoundly so that the molecule as a whole starts to move for a time τ_1'. During τ_0' the molecular center of gravity vibrates and during τ_1' it performs simple diffusion. In a low-viscosity liquid (for example, without hydrogen bonding) the vibrational period τ_0' never exists and the molecule was supposed to perform a continuous diffusion. Intermediate cases will occur. The motion of the center of gravity occurs simultaneously with the proton motion with respect to the center of gravity. Only cases for which $\tau_1 \ll \tau_0$ were considered, which means that the rotations

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[1] *Proceedings of the Chalk River Symposium on Inelastic Scattering of Neutrons in Solids and Liquids* (Internatonal Atomic Energy Agency, Vienna, 1963); *Proceedings of the Vienna Symposium on Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1961); *Proceedings of the Bombay Symposium on Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1965).

[2] *Thermal Neutron Scattering*, edited by P. A. Eglestaff (Academic Press Inc., New York, 1965), Chaps. 7 and 8.

[3] V. F. Turchin, *Slow Neutrons* (Oldbourne Press, London, 1965).

[4] P. D. Randolph and K. S. Singwi, Phys. Rev. **152**, 99 (1966).

[5] K. Sköld and K E. Larsson, Phys. Rev. **161**, 102 (1967).

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

[7] K. E. Larsson, L. Queiroz do Amaral, N. Ivantchev, S. Ripeanu, L. Bergstedt, and U. Dahlborg, Phys. Rev. **151**, 126 (1966).

[8] K. E. Larsson and L. Bergstedt, Phys. Rev. **151**, 117 (1966).

must be hindered so that rotational jumps have a meaning.

This simple physical picture, when treated in the van Hove formalism and by use of methods developed by Singwi and Sjölander,[9] leads to a prediction of an observable quantity: the full width $\Delta\omega$ of the quasi-elastic neutron peak as a function of κ^2, where $\hbar\kappa$ is the momentum transfer in the scattering process. Of particular interest is the asymptotic behavior of $\Delta\omega$ for large and small values of κ.

For a small self-diffusion coefficient D and large values of κ, $\Delta\omega$ is predicted to be independent of κ and determined by $1/\tau_1$. For small values of κ, $\Delta\omega$ is essentially determined by

$$2''D''\kappa^2=2\left(\frac{\langle l_x^2\rangle}{2\tau_0}+\frac{\langle r_i^2\rangle}{6\tau_0}\right)\kappa^2,$$

where $3\langle l_x^2\rangle=\langle l^2\rangle$ and $\langle r_i^2\rangle$ is the mean-square radius of the thermal cloud set up by the proton.

For a large self-diffusion coefficient and larger values of κ, $\Delta\omega$ is predicted to vary as $1/\tau_0+D\kappa^2$, and for small values of κ as

$$2\left(D+\frac{\langle l_x^2\rangle}{2\tau_0}+\frac{\langle r_i^2\rangle}{6\tau_0}\right)\kappa^2=2''D''\kappa^2.$$

In the first two experimental cases[7] analyzed along these lines—namely, normal propanol C_3H_7OH, and pentane C_5H_{12}—a satisfactory fit to the neutron-scattering data was obtained. When, however, the same model was tried on glycerol $C_3H_5(OH)_3$, it proved to be impossible to fit the given formulas to certain linewidth results obtained at 334 and 369°K (compare Ref. 6, Fig. 6). The characteristics of these two linewidth curves were that in spite of the fact that the true self-diffusion coefficient D is very small at these temperatures, the curves do not seem to reach a κ-independent asymptote for larger values of κ but instead to reach a sloping asymptote typical for a case when diffusion is important.

On the basis of this observation a slight modification of the earlier model is done as well as a sharper definition of the various possibilities for proton motion relative to the center of gravity.

A slightly revised mathematical form of the neutron cross section follows from the change of the physical background. The new expressions for linewidths are fitted to the experimental results on glycerol and normal propanol. The new analysis gives a satisfactory fit to the data over the whole temperature range investigated which is from 266 to 453°K for glycerol and from 153 to 323°K for normal propanol.

Comparison of the results to data obtained from dielectric and ultrasonic relaxational studies shows qualitative and in some cases even quantitative agreement. It must be pointed out that simple exponential autocorrelation functions for linear and rotational velocities most probably do not exist in liquids or in any condensed system for short times.

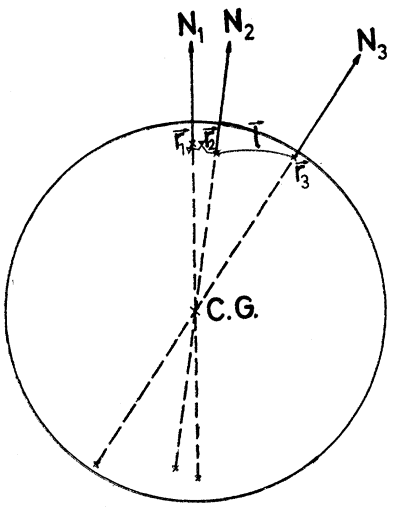

FIG. 1. Illustration of the motion of the molecule relative to its center of gravity: N_1 is the molecular direction at time $t=0$; N_2 is the molecular direction at time $t=\tau_0$. In between these positions the direction diffuses randomly. A proton sitting at $\mathbf{r}_1$ at time $t=0$ diffuses and vibrates until it reaches position $\mathbf{r}_2$. N_3 is molecular direction after jump. A proton starting at $\mathbf{r}_1$ is dragged with the molecule in its directional change to the position $\mathbf{r}_3$. The jump length l is covered in time τ_1.

II. MODEL

The molecules considered consist of carbon chains with protons and hydroxyl groups hooked on to the chain. Thus the molecule is visualized as a line with protons hooked on at selected positions. The motion of this "line" molecule, with respect to the center of gravity, is described (Fig. 1) in the following way:

At time $t=0$ the molecule has the direction in space given by N_1. A proton sitting at $\mathbf{r}_1$ vibrates around a quasiequilibrium position, which in itself performs simple diffusive motion. The diffusive motion by small steps, which gradually changes the molecular direction in space, is described by a diffusion coefficient D_p, and goes on until the average time $t=\tau_0$. At this time the molecular direction has changed from N_1 to N_2 resulting in a displacement of the equilibrium position of the regarded proton from $\mathbf{r}_1$ to $\mathbf{r}_2$.

The physical cause for these small displacements is small changes in the orientations of neighbor molecules. After the elapse of the average time τ_0 the molecular direction in space changes abruptly from N_2 to N_3 in a short time τ_1. This large change of molecular orientation transfers the considered proton from $\mathbf{r}_2$ to $\mathbf{r}_3$, a distance l, which is the jump length. The physical cause for this larger change of the molecular orientation is a larger change of the position or orientation of neighbor molecules. The equivalent to a sudden change of molecular orientation would be a partial rotation resulting in iso-

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[9] K. S. Singwi and A. Sjölander, Phys. Rev. **119**, 863 (1960).

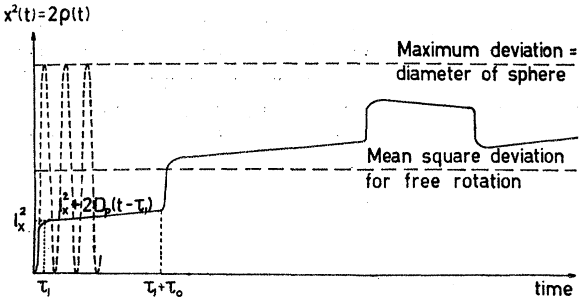

FIG. 2. A component $x^2(t)$ of the square deviation of one selected proton from an origin for the case of hindered rotation (solid line) and free rotation (dashed line). For free rotation the time $\tau_0=0$ and the mean-square deviation is of the order of the molecular radius for rotation. For hindered rotation $\tau_0 \gg \tau_1$ and the mean-square deviation l_x^2 for one jump is in general smaller than for free rotation. The long time average for the hindered rotation involving a large number of jumps is equal to the mean-square deviation for free rotation. The gradual diffusion of molecular direction causes the mean-square deviation for one jump to increase linearly in the period from τ_1 to $\tau_1+\tau_0$. When $\tau_0=0$ the hindered rotation curve transforms to the free-rotation curve.

meric molecular form. After the average time $\tau_0+\tau_1$ the whole procedure is repeated again. The motion of the center of gravity is described *either* as a vibrational state in case the molecule is bound to neighbors for the time τ_0', which ought to be very long in the solid state, *or* as a diffusive state for the time τ_1'. The displacement of the center of gravity is then described by $\langle \Delta x_{\mathrm{c.g.}}^2 \rangle = 2D\tau_1'$. A mixture of the two cases might occur even in hydrogen-bonded liquids at higher temperatures. At the end of the average time τ_0', which might be much longer than $\tau_0+\tau_1$, the molecular configuration around the regarded molecule has changed so much that the molecule may be regarded free to diffuse for the time τ_1' to another position where it is again caught in a quasistable position.

Here the discussion has been concerned with only one proton. The same discussion can of course be carried through for each proton in the complex molecule. The neutron-scattering picture will be the average of all protons in the molecule.

III. CROSS SECTION FOR QUASI-ELASTIC NEUTRON SCATTERING

The derivation of the cross section for the quasi-elastic scattering corresponding to the physical model outlined in Sec. II follows closely the derivation given in the earlier work.[8] The motion is naturally divided into steps which for the motion of the center of gravity are simple and the same as those used in the earlier derivation and first derived by Singwi and Sjölander[9]: a vibratory period τ_0' followed by a diffusive period τ_1'. Here $\tau_0' \gg \tau_1'$ for strongly bound molecules (solidlike behavior) and $\tau_1' \gg \tau_0'$ for simple diffusive behavior.

Simultaneously with the motion of the center of gravity a motion relative to it occurs which is assumed to be of rotational character. As illustrated in Fig. 1, this motion is supposed to occur on the surface of a sphere. One sphere is to be imagined for each proton with distance r_{j0} from the center of gravity. The motion is supposed to have one diffusive-vibrational period τ_0 and one jump period τ_1.

The displacement of the proton on the surface of the sphere (which is the relative motion) may in this model be visualized as is shown in Fig. 2. In the short time τ_1 the proton is displaced from $\mathbf{r}_2$ to $\mathbf{r}_3$ in a rotational jump. Different jump lengths are supposed to be possible with a root-mean-square value $\langle l_x^2 \rangle^{1/2}$ of one of its components. Starting out from this new position at $\mathbf{r}_3$ a vibratory-diffusive displacement occurs for the time τ_0, for the present purpose supposed to be considerably longer than τ_1. During the time from τ_1 to $\tau_1+\tau_0$ the displacement of the proton from $\mathbf{r}_3$ slowly increases due to small gradual changes of the molecular orientation, i.e., due to diffusive rotation. At the time $\tau_1+\tau_0$ the procedure is repeated again and so on. It is to be noticed however, that the proton motion is bounded to the surface of the sphere and therefore the displacement can never exceed a value determined by the diameter of the sphere. The displacement after many jumps might look somewhat like the one illustrated in Fig. 2. This displacement is to be compared with a free rotation, which is periodic and corresponds to the case that $\tau_0 \to 0$. In this paper we shall only deal with the hindered rotations for which $\tau_0 \gg \tau_1$. It is shown that it is the existence of the delay time τ_0 which is the main cause of the line broadening in quasi-elastic neutron scattering. For free rotation no broadening will occur but instead a large Debye-Waller factor will govern the intensity. It is also obvious that the mean-square deviation for very long observation times is equal for the hindered and free rotation. In the actual neutron observation the small values of κ necessary to reach this condition of "long times" are not obtained and it is the effect of one jump, which is observed (for $\tau_0 \gg \tau_1$).

The relative proton motion during the time τ_0 is now described by a function $g_i(\mathbf{r},t)$ which describes the probability of finding the particle in position $\mathbf{r}$ at the time t, if it started out from some origin at the time 0. As the proton vibration occurs around an instantaneous quasiequilibrium position defined by diffusion on the surface of the sphere of Fig. 1 an appropriate definition of $g_i(\mathbf{r},t)$ is

$$g_i(\mathbf{r},t)=\int g_{i\,\mathrm{diff}}(\mathbf{r}',t)g_{i\,\mathrm{vib}}(\mathbf{r}-\mathbf{r}',\,t)d\mathbf{r}', \qquad (1)$$

where $\mathbf{r}'$ is the instantaneous position of the center of vibration of the proton, $\mathbf{r}-\mathbf{r}'$ is the instantaneous relative position of the proton with respect to this center of vibration, and $\mathbf{r}$ is the coordinate of the proton. Here $g_{i\mathrm{diff}}(\mathbf{r},t)$ describes the diffusive motion and $g_{i\mathrm{vib}}(\mathbf{r}-\mathbf{r}',t)$ the vibration around the instantaneous quasiequilibrium position.

In the present model it would be appropriate to find $g_{i\,\mathrm{diff}}(\mathbf{r}',t)$ from a solution of a diffusion equation

$$\partial g_{i\,\mathrm{diff}}(r_{j0},\Theta,\varphi,t)/\partial t = D_p \Delta g_i(r_{j0},\Theta,\varphi,t)\,, \tag{2a}$$

where D_p describes the proton diffusion on the surface of the sphere, r_{j0} is the distance of the considered proton from the effective center of gravity of the molecule, and Θ and φ are the polar angles determining the instantaneous direction of the molecule between N_1 and N_2 in Fig. 1. The treatment is equivalent to the one given by Debye[10] in his theory of dielectric absorption and dispersion. The same problem was also treated, for instance, by Blombergen[11] in his work on nuclear magnetic resonance.

The solution of this equation with the proper boundary condition is given as a series of spherical harmonics $P_l(\cos\Theta)$

$$g_{i\,\mathrm{diff}}(r_{j0},\Theta,\varphi,l) = \frac{1}{4\pi r_{j0}{}^2} \sum (2l+1) P_l(\cos\Theta) e^{-D_p l(l+1)t/r_{j0}{}^2}\,. \tag{2b}$$

This solution gives, however, a rather unsurveyable final cross-section result. Therefore an approximate description of the motion of the considered proton on the surface of the sphere is tried. It seems clear from the experiment that the distance $\mathbf{r}_2-\mathbf{r}_1$ in Fig. 1 travelled by the proton in the time τ_0 is small; i.e., the angle Θ remains small. Therefore the sphere is approximated by a plane surface around the direction N_1. To simplify further, the solution of an infinite plane surface is tried for $g_{i\,\mathrm{diff}}(\mathbf{r}',t)$:

$$g_{i\,\mathrm{diff}}(r',t) = (1/4\pi D_p t) e^{-(r')^2/4D_p t}\,, \tag{2c}$$

where $r' = (x^2+y^2)^{1/2}$ is the distance from $\mathbf{r}_1$ to the intersection of the instantaneous molecular direction line with the tangent plane at $\mathbf{r}_1$.

The accuracy of this approximation is tested by comparing the forms of $g_{i\,\mathrm{diff}}(r',t)$ from Eqs. (2b) and (2c). A calculation of $g_{i\,\mathrm{diff}}(r',t)$ from Eq. (2b) was made by a computer for various values of t and compared to the solution (2c). It is found that the shapes given by Eqs. (2b) and (2c) agree quite accurately (to within $\pm 1\%$) over the most important region of r'-values, if D_p is taken in the range (0.1–0.5). 10^{-5} cm^2/sec, and if the radius r_0 at which the proton is moving is taken as 1–3 Å. Only for r' values corresponding to a displacement approaching one diameter of the sphere the deviation is larger.

This approximate form for $g_{i\,\mathrm{diff}}(r',t)$ is thus adopted and the function $g_{i\,\mathrm{vib}}(\mathbf{r}-\mathbf{r}',t)$ is taken as

$$g_{i\,\mathrm{vib}}(r-r',\,t) = \frac{1}{(4\pi\rho(\infty))^{3/2}} e^{-(r-r')^2/4\rho(\infty)}\,, \tag{2d}$$

where $\rho(\infty) = \frac{1}{6}\langle r_i{}^2\rangle$ and defines the mean-square radius of the vibrational cloud. The extra folding that is thus introduced in the cross-section definition is easily evaluated by using the methods of the earlier work.[8]

In order to describe the second kind of relative proton motion, which is the jump motion from $\mathbf{r}_2$ to $\mathbf{r}_3$ in Fig. 1, it is of interest to make a comparison with the expression (2d) for the vibrational motion. The assumption justifying Eq. (2d) is that the motion continues for a time τ_0 ,which is supposed to be long compared to the rise of the width function $\rho(t)$ occuring in a time of the order of 10^{-14} sec. This rise may be approximated by the form $\rho(t) = \frac{1}{2}(v_x t)^2$. However, after about 10^{-14} sec $\rho(t)$ is supposed to flatten out and assume its constant value $\rho(\infty)$.

In the jump motion the situation is somewhat similar. The jump is supposed to occur for a very short time (of the order of 10^{-13} sec) whereafter the new quasiequilibrium position described by Eq. (1) is established. The probability of still finding the proton in a jumping state is supposed to be e^{-t/τ_1}, where τ_1 is of the order of 10^{-13} sec. Therefore the rise and the first part of the width function $\rho(t)$ (Fig. 2) are important. Nothing, however, is known about the nature of the jump motion. If it were supposed that the proton moved in a periodic potential $V(r)$, which was constant during the jump, one would have $\partial V/\partial r = 0$. Consequently the proton would move like a gas particle and therefore $2\rho(t) = (v_x t)^2$. This is equivalent to assuming that the molecule performs a free rotation with an angular velocity Ω in such a way that the proton at a distance r_{j0} from the center of gravity is displaced a distance $r_{j0}\Omega t$ in the time t. Because of the lack of knowledge of the details of the potential, this form is used. If the average jump time is τ_1 and a root-mean-square jump velocity $\langle v^2\rangle^{1/2}$ is used to define v_x, the product $v_x\tau_1$ is a component l_x of the jump length l.

Concerning the space distribution of jumps the same considerations should be given to it as was given to the diffusive-vibrational motion: the jumps occur on the surface of a sphere. In order to simplify the treatment to the same degree as was done by replacing Eqs. (2b) by (2c) the spherical surface is replaced by a tangent plane to the sphere at $\mathbf{r}_2$ in Fig. 1. The jumps are supposed to occur in random directions in the plane but may, for each proton (j) which is considered, have an average value l_j. Only the average value of the jump length for the various protons will be considered. The function describing the spreading out of the proton during the jump is taken as $h_i(\mathbf{r},t)$. If the jump motion starts from an origin at the time $t=0$, then $h_i(\mathbf{r},t)$ gives the probability of finding the particle at the position $\mathbf{r}$ at the time t. A Gaussian form is taken for $h_i(\mathbf{r},t)$, which therefore is given by

$$h_i(r,t) = \frac{1}{2\pi(v_x t)} e^{-r^2/2(v_x t)^2}\,, \tag{3}$$

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[10] P. Debye, *Polar Molecules* (Dover Publications, Inc., New York, 1945), particularly Chap. 5.

[11] N. Bloembergen, *Nuclear Magnetic Relaxation* (W. A. Benjamin, Inc., New York, 1961); see particularly Chap. 4.

where $r=(x^2+y^{2\prime})^{1/2}$ is a distance in the tangent plane at $\mathbf{r}_2$.

The evaluation of the cross section shows[8] that the essential feature of the jump motion is the jump length and that for smaller values of κ, or when $v_x\tau_{10}\kappa$ or $v_x\tau_{11}\kappa<1$ it is allowed to replace v_xt with $v_x\tau_1=l_x$ in the formula (3) [compare Eqs. (18), (20), and (27) combined with Fig. 1 of Ref. 8]. The effect of the jump is then similar to the introduction of a Debye-Waller factor which may be understood because the jump is supposed to be followed by a semistable dynamic situation for the relatively long time τ_0.

Another and even more simplified treatment of the jump problem would be to assume $h_i(r,t)$ time independent and put $h_i(r)=\delta(r-l)$. At the same time the probability of finding a proton in a jump motion should be changed from $q_i(t)=e^{-t/\tau_1}$ to $q_i(t)=1$. This means that the jump is considered instantaneous. The resulting cross section will then change slightly as will be pointed out below.

The two relations (1) and (3), with $g_{i\,\mathrm{diff}}(r,t)$ determined by Eq. (2c) and $g_{i\,\mathrm{vib}}(r,t)$ by Eq. (2d), are used to describe the motion of a selected proton with respect to the molecular center of gravity. It should be noted that these simplifications restrict the use of the present formulas to cases where rotations are hindered, or in general to liquids with viscosities (>1cP) so that rotational jumps have a meaning. This implies that $\tau_1\ll\tau_0$ in all cases considered here. If $\tau_0\rightarrow 0$ such that $\tau_1>\tau_0$, the rotational motion tends to be free. If $\tau_0=0$ the rotation is a free one, and we are dealing with a liquid for which the viscosity is in general <1 cP. This case is not considered in the present work.

With these assumptions the resulting cross sections for incoherent quasi-elastic neutron scattering are (the detailed balance factor left out):

(a) τ_0' and $\tau_0\gg\tau_1'$: high-viscosity liquid or solid.

$$\frac{d^2\sigma}{d\Omega d\omega}=\frac{a^2}{\pi}\frac{k}{k_0}\tau_{00}$$

$$\times\frac{e^{-2W_i-2W_e}(1+D\tau_0'\kappa^2)[1+\frac{2}{3}D_p\tau_{00}\kappa^2-(\tau_{00}/\tau_0)e^{-2W_i-4W_e-(1/6)<l^2>\kappa^2}]-(\tau_{00}/\tau_0')e^{-4W_i-2W_e}}{\{(1+D\tau_0'\kappa^2)[1+\frac{2}{3}D_p\tau_{00}\kappa^2-(\tau_{00}/\tau_0)e^{-2W_i-4W_e-(1/6)<l^2>\kappa^2}]-(\tau_{00}/\tau_0')e^{-4W_i-2W_e}\}^2+(\omega\tau_{00})^2(1+D\tau_0'\kappa^2)^2}. \quad (4)$$

The notations are the same as those previously[8] used, namely: a is the incoherent scattering length; $\mathbf{k},\mathbf{k}_0$ are the scattered and ingoing neutron wave vectors; $\tau_{kl}^{-1}=\tau_k^{-1}+\tau_l'^{-1}$, k, $l=0$, 1; $2W_i=\frac{1}{6}\langle r_i^2\rangle\kappa^2$, where $\langle r_i^2\rangle$ is the mean-square radius of the thermal cloud set up by a vibrating proton relative to the molecular center of gravity; $2W_e=\frac{1}{6}\langle r_e^2\rangle\kappa^2$, where $\langle r_e^2\rangle$ is the mean-square radius of the thermal cloud of a proton due to vibrations of the center of gravity. Normally $\langle r_e^2\rangle\ll\langle r_i^2\rangle$. D is a self-diffusion coefficient; D_p is a diffusion coefficient describing the diffusive motions of the direction of the molecular axial symmetry line. Only two degrees of freedom are connected with this motion in the present approximation; $\langle l^2\rangle=2\langle l_x^2\rangle$ is the mean square of the jump length of all the protons in the molecule due to a sudden directional change of the axial symmetry line. As the motion occurs in a plane there are only two degrees of freedom for the motion. The linewidth is given by

$$\Delta\omega=\frac{2}{\tau_{00}}\biggl[1+\tfrac{2}{3}D_p\tau_{00}\kappa^2-\frac{\tau_{00}}{\tau_0}$$
$$\times e^{-2W_i-4W_e-(1/6)l^2\kappa^2}-\frac{\tau_{00}}{\tau_0'}\frac{e^{-4W_i-2W_e}}{1+D\tau_0'\kappa^2}\biggr]. \quad (5a)$$

For large values of κ there is no horizontal tangent to the curve $\Delta\omega=f(\kappa^2)$ but the linewidth asymptotically approaches the form

$$\Delta\omega=2\left(\frac{1}{\tau_{00}}+\tfrac{2}{3}D_p\kappa^2\right). \quad (5b)$$

For small values of κ one finds

$$\Delta\omega=2\left[D+\tfrac{2}{3}D_p+\frac{\langle r_i^2\rangle}{6\tau_0}+\frac{\langle l^2\rangle}{6\tau_0}+\frac{\langle r_i^2\rangle}{3\tau_0'}\right]\kappa^2$$
$$=2(D_{\mathrm{c.g.}}+D_{\mathrm{rel}}+D_{\mathrm{mix}})\kappa^2=2''D''k^2, \quad (5c)$$

where $D_{\mathrm{c.g.}}=D$, and $D_{\mathrm{rel}}=\frac{2}{3}D_p+\langle r_i^2\rangle/6\tau_0+\langle l^2\rangle/6\tau_0$ is a fictitious diffusion coefficient describing the motion of the average proton relative to its molecular center of gravity. $D_{\mathrm{mix}}=\langle r_i^2\rangle/3\tau_0'$ is a mixture term between the relative motion and the center-of-gravity motion.

(b) $\tau_1'\gg\tau_0'$ and τ_0: low-viscosity liquid.

$$\frac{d^2\sigma}{d\Omega d\omega}=\frac{a^2}{\pi}\frac{k}{k_0}\tau_0e^{-2W_i}$$
$$\times\frac{1+(D+\frac{2}{3}D_p)\tau_0\kappa^2-e^{-2W_i-(1/6)<l^2>\kappa^2}}{[1+(D+\frac{2}{3}D_p)\tau_0\kappa^2-e^{-2W_i-(1/6)<l^2>\kappa^2}]^2+(\omega\tau_0)^2}. \quad (6)$$

The linewidth is given by

$$\Delta\omega=\frac{2}{\tau_0}(1+(D+\tfrac{2}{3}D_p)\tau_0\kappa^2-e^{-2W_i-(1/6)<l^2>\kappa^2}). \quad (7a)$$

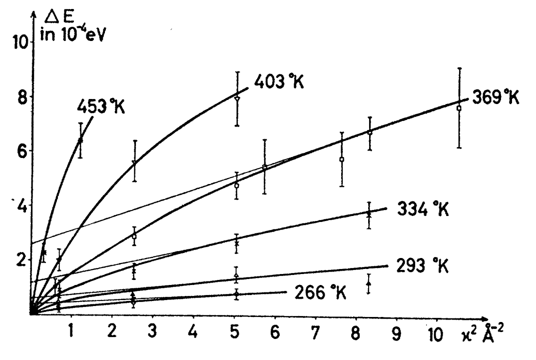

FIG. 3. Observed linewidth data on glycerol together with fitted theoretical linewidth forms given as solids lines. The best fit to the asymptotic behavior is shown for 266, 293, 334, and 369°K. The intercept on the ΔE axis is $2\hbar/\tau_{00}$. The slope of the asymptote is $2\hbar D_p$.

For large values of κ the asymptotic form is

$$\Delta\omega = 2[1/\tau_0 + (D + \tfrac{2}{3}D_p)\kappa^2]. \tag{7b}$$

When κ is small the asymptotic form is

$$\Delta\omega = 2\left(D + \tfrac{2}{3}D_p + \frac{\langle r_i^2\rangle}{6\tau_0} + \frac{\langle l^2\rangle}{6\tau_0}\right)\kappa^2 = 2(D_{\text{c.g.}} + D_{\text{rel}})\kappa^2. \tag{7c}$$

The slope of the linewidth curves at the origin is thus determined by a combination of a relative and a center-of-gravity diffusion coefficient.

If the jump motion had been described by a form

$$\frac{1}{n}\sum_{j=1}^{n}\delta(r - l_j),$$

where l_j is the length of the jump of proton j, a slightly different cross section would be the result. Everywhere in Eqs. (4)–(7) the factor $e^{-(1/6)\kappa^2\langle l^2\rangle}$ would have been replaced by a factor

$$\frac{1}{n}\sum_{j=1}^{n}\frac{\sin\kappa l_j}{\kappa l_j}.$$

In practice the difference between the two resulting cross sections is very small. The most important simplification made in the derivation of Eqs. (4)–(7) is to replace $v_x t$ by $v_x\tau_1 = l_x$. If $v_x t$ is kept in Eq. (3) the exact final cross section is of non-Lorentzian form.

IV. FIT TO GLYCEROL DATA

As already described earlier,[6] slow-neutron-scattering experiments were performed on glycerol in the temperature range 266–453°K. Within this temperature range the viscosity varies between 230 P and 2.1 cP, respectively. Experimentally the analyzer resolution was 0.2 meV at 4 Å, the neutron wavelength at which the quasi-elastic line broadening was studied. Linewidth data were extracted from the experiment and these data will now be used for fitting the model mainly by use of Eqs. (5a)–(5c). The basic assumption is that a separation of the quasi-elastic peak from the inelastic background can be made. A change of the linewidth values due to another separation hypothesis may change the values of some of the parameters given below but will probably not change the basic results.

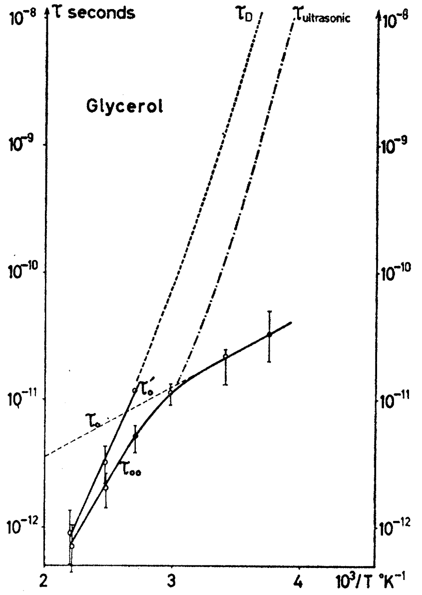

FIG. 4. Relaxation times τ_{00}, τ_0, and τ_0' for glycerol derived from the neutron data. The observed dielectric and ultrasonic relaxation times are shown as dashed and dash-dot lines, respectively. Part of the dielectric data are extrapolated by use of a formula proposed by McDuffie and Litowitz.

The analysis was started at the temperatures 334 and 369°K, where it is clearly seen that no horizontal saturation value is approached (Fig. 3). A tangent is drawn to the curves at larger values of κ. Its intersection with the $\Delta\omega$ axis gives $2/\tau_{00}$ and its slope gives $\frac{4}{3}D_p$. It is, however, necessary to know the division of τ_{00} into τ_0 and τ_0'. To get an idea of this division an analysis of the data at 266 and 293°K was tried. It was found that values of D_p and τ_{00} could be obtained within rather large limits of error. At these low temperatures $\tau_{00} \simeq \tau_0$ and therefore, if $\log_{10}\tau_0$ is plotted as a function of $1/T$, one may search for a simple way to extrapolate the curve to higher temperatures (lower values of $10^3/T$, compare Fig. 4). A straight-linear extrapolation is tried and seems reasonable. It thus seems probable that $\tau_{00} \simeq \tau_0$ at 266, 293, 334°K within the present limits of error. Already at $T = 369$°K a division into two components according to $\tau_{00}^{-1} = \tau_0^{-1} + \tau_0'^{-1}$ is necessary and also possible as both τ_{00} and τ_0 are known.

With these parameters known the only unknown factor is the jump length $\langle l^2\rangle$, because D is calculated by use of the Stoke-Einstein formula from the measured[12] values of the coefficient of viscosity η. By use of formula (5a) a fit to the data is made from which $\langle l^2\rangle$ is obtained.

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[12] R. Piccirelli and T. A. Litowitz, J. Acoust. Soc. Am. **29**, 1009 (1957).

Table I. Result of the analysis of the neutron data on glycerol.

T (°K)	τ_{00} (10^{-12} sec)	τ_0 (10^{-12} sec)	τ_0' (10^{-12} sec)	D[a] (10^{-5} cm^2/sec)	D_p (10^{-5} cm^2/sec)	$\langle l^2 \rangle$ (Å^2)	$\frac{1}{6}\langle r_i^2 \rangle$ (Å^2)
266	33	33			0.095	2.46	0.07
293	22	22		0.008	0.18	2.79	0.08
334	11.3	11.3		0.013	0.36	2.67	0.12
369	5.1	9	11.8	0.064	0.89	2.40	0.14
403	2.1[b]	5.8[c]	3.2[b]	0.2	0.9[c]		0.16
453	0.7[b]	4.0[c]	0.9[b]	0.6	1.5[c]		0.20
					Mean value	2.6	

[a] Self-diffusion coefficient calculated from the Stoke-Einstein formula, $D=k_BT/6\pi r\eta$, and measured values of η.

[b] Value of τ_0' determined from the values of "D" obtained directly from the neutron linewidths at 403 and 453°K. Thereafter τ_{00} is derived.

[c] Values of D_p obtained by extrapolation of the relation $D_p=D_{p0}e^{-E/k_BT}$ with $E=3.6$ kcal/mole.

The complete result of this analysis is shown by the first four lines of Table I. It is seen that $\langle l^2 \rangle$ comes out const$=2.6$ Å^2 within limits of error.

The data at higher temperatures 403 and 453°K do not permit a determination of a tangent giving D_p and τ_{00}. To avoid this dilemma use is made of the slope at the origin of these line width curves. This slope is theoretically determined by the relation (5c) as $2(D_{\text{c.g.}}+D_{\text{rel}}+D_{\text{mix}})$. If $\langle l^2 \rangle$ is assumed to be the same for all temperatures the only unknown is τ_0' which may thus be obtained. It is also necessary to know D_p at 403 and 453°K. These two values of D_p are obtained by extrapolation of a plot of $\log_{10}D_p$ versus $1/T$ and are given in Table I. This extrapolation may be done because D_p is known at 369, 334, 293, and 266°K. As τ_0' is thus known and τ_0 is assumed known from extrapolation of the curve $\log_{10}\tau_0$ versus $10^3/T$ the variable τ_{00} may be calculated. The results of this analysis are given on lines 5 and 6 of Table I.

Figure 4 give the complete result for the obtained relaxation times τ_0', τ_0, and τ_{00}. It is of great interest to compare these results to those obtained by other experimental methods. In the figure, results obtained in dielectric relaxation time studies by McDuffie and Litowitz[13] are shown up to 285°K. The times given are the average relaxation time values τ_{av} derived by these authors. They have also given a formula which describes the temperature dependence of τ_{av} very well.[14] If this formula is also used for higher temperatures, it is found that the present τ_0' values very nicely fall on this extrapolated line. As the dielectric relaxation time should depend upon changes of molecular orientations, particularly of the OH groups, this coincidence is very gratifying. The present values of τ_0' were already as a starting assumption assumed to be associated with the breakage of *all* the hydrogen bonds to neighbor molecules so that a new orientation of the whole molecule is brought about.

It is of interest to notice that within the temperature ranges valid for this experiment both τ_0' and τ_0 may be given as exponential functions $\tau=c\exp(E/k_BT)$. It is found that within the temperature ranges investigated here the activation energies are (10 ± 3) kcal/mole for τ_0' and $(2.6)\pm1)$ kcal/mole for τ_0.

It is also interesting to notice that Davidson and Cole[15] report the existence of a high-frequency dielectric relaxation in glycerol. This much shorter relaxation time could possibly be associated with τ_0 in the present notation and could be caused by isomeric rotations of CH_2OH groups or other changes of direction of *one* hydrogen bond.

It is also of interest to compare the present neutron data to ultrasonic relaxation times derived by Piccirelli and Litowitz.[12] These authors find a broad distribution of relaxation times for glycerol, and the relaxation time τ_s' corresponding to the peak of the distribution is given in Fig. 4. It is seen that the mechanical studies apparently gives something different from the neutron and dielectric relaxation time studies. τ_s' is more in agreement with the present τ_{00} for the highest temperatures, which is to be considered as a mean value over two possible relaxation processes.

It is finally of interest to compare the calculated values of "D"$=D_{\text{c.g.}}+D_{\text{rel}}+D_{\text{mix}}$ with those directly obtained from the observed slope at the origin of the linewidth curves. In calculating "D", all the analyzed data presented in Table I were used. As shown in Fig. 5 the sum of the calculated components agrees very well with the directly observed slope of the linewidth curves

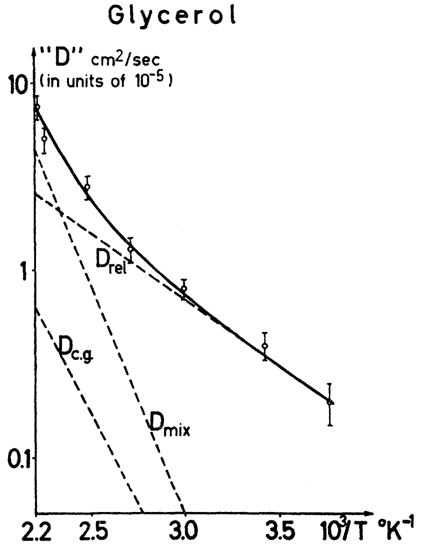

Fig. 5. Observed diffusion coefficient "D". The various theoretical components D, D_{mix}, and D_{rel} are shown as dashed lines. The full line is the sum of these components.

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[13] G. E. McDuffie, Jr., and T. A. Litowitz, J. Chem. Phys. **37**, 1699 (1962).

[14] $\tau_{\text{av}}=\beta\tau_0$, where β is a measure of the width of the distribution of relaxation times. β varies with temperature and it has been assumed here that β varies from 0.7 to 0.9 in the temperature range from +12 to +180°C.

[15] D. W. Davidson and R. H. Cole, J. Chem. Phys. **19**, 1484 (1951). R. H. Cole and D. W. Davidson, J. Chem. Phys. **20**, 1389 (1952).

TABLE II. Result of the analysis of neutron data on *n*-propanol

T	τ_{00} (10^{-12} sec)	τ_0 (10^{-12} sec)	τ_0' (10^{-12} sec)	D^{a} (10^{-5} cm^2/sec)	D_p (10^{-5} cm^2/sec)	$\frac{1}{6}\langle r_i^2\rangle$ (Å^2)	$\langle l^2\rangle$ (Å^2)
153	18	18				0.069	7.5
173	12	12				0.10	8.1
233	7.6	7.6		0.08	0.18	0.14	7.5
263	5.2	6.1	35	0.24	0.29	0.15	7.8
293	3.6	5.2	11.7	0.58	0.52	0.19	9.3
						Mean value	8.1±0.6

[a] From observations of J. R. Partington, R. F. Hudson, and K. W. Bagnall, J. Chem. Phys. 55, 77 (1958).

at the origin. The derived quantities given in Table I form a consistent set of parameters.

V. FIT TO NORMAL PROPANOL DATA

In an earlier work[7] an analysis was made of neutron-scattering data from propyl alcohol in the temperature range from 153 to 233°K. A critical test of the fit possible to obtain with the previous[8] model to the linewidth data at the lowest temperatures indicates that the fit is not perfect. Therefore, an attempt was made to use the revised version of cross sections and linewidth formulas given in the present paper to fit to the propyl alcohol data. The analysis is carried out in a similar fashion as already described for glycerol. Use is made of formula (5a) at temperatures 153, 173, 233, 263, and 293°K. The complete result of the analysis is given in Table II. Revised values are obtained for the jump length[16] $\langle l^2\rangle$ as well as for the relaxation times τ_{00}, τ_0, and τ_0'. As shown in Fig. 6 the main features remain, however, the same as in the earlier analysis.

It is again of great interest to compare the relaxation times resulting from the analysis of the neutron data with those obtained from dielectric and ultrasonic relaxation-time studies. Dielectric relaxation in *n*-propanol was studied by Davidson and Cole.[15] These authors state that the main relaxation which they observe in their frequency range corresponds to a single relaxation time and not to a distribution of times as for glycerol. They observe, however, a high-frequency component which they divide into two components, one with relaxation times about 200 times shorter than the primary one, and another with relaxation times considerably shorter and with a different temperature dependence than the others. In Fig. 6. the main dielectric relaxation τ_D as well as the intermediate τ_D' which is taken as 200 times shorter than τ_D are given. It is seen that the intermediate relaxation time τ_D' and the neutron time τ_0' agree in a qualitative sense and probably even agree within limits of error. The third, highest-frequency dielectric relaxation could very well be identical with the present τ_0. τ_0 may very well be associated with directional changes of the C-C-C line of the molecule, whereas τ_0' should correspond to the breakage or other change of the hydrogen bond so that the direction of the OH group undergoes a major change.

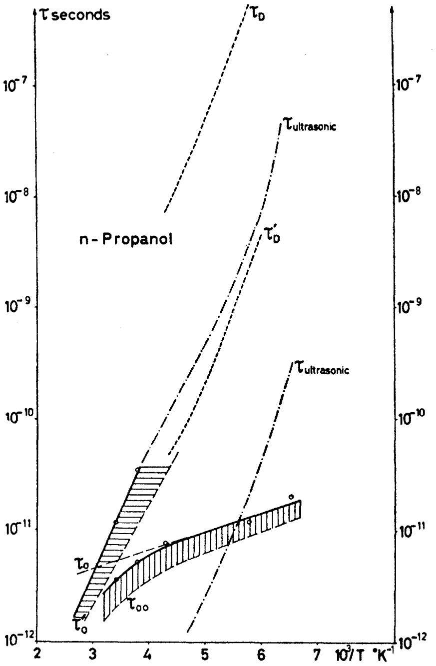

FIG. 6. Relaxation times τ_{00}, τ_0, and τ_0' for *n*-propanol derived from the neutron data. The present cross-section forms (solid lines) as well as the earlier ones (dashed lines) were used for analysis. The hatched areas show the regions within which the values of τ_{00} and τ_0' may fall. The observed dielectric relaxation times τ_D and τ_D' are shown as dotted lines. The limits, between which reported ultrasonic relaxation times fall, are shown as dash-dot lines.

In ultrasonic-relaxation-time studies on propanol by Lyon and Litowitz[17] a broad distribution of relaxation times is derived approximately between the limits given in Fig. 6. It is seen that the proposed upper limit for $\tau_{\text{ultrasonic}}$ happens to agree with the present τ_0'. If for instance both the relaxation processes described by τ_0' and τ_0 participate in the ultrasonic relaxation one would expect that a phenomenological explanation of the type proposed by Lyon and Litowitz has to result in a broad distribution of relaxation times. There is thus a qualitative agreement between the neutron and mechanical relaxation-time studies.

VI. MAIN FEATURES OF THE ANALYSIS

It is of interest to compare the magnitude of the various displacements of a proton bound in a complex molecule. The displacements of interest are given by: $\langle\Delta x_p^2\rangle = 2D_p\tau_{00}$ is the diffusive directional change of the molecule with respect to the center of gravity. The diffusion occurs in small steps. $\langle l_x^2\rangle = \frac{1}{2}\langle l^2\rangle$ is a mean-square component for the jump length. The diffusion occurs in large steps. $\frac{1}{3}\langle r_i^2\rangle$ is a mean-square component

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[16] In the previous papers (Refs. 7 and 8), $\langle l^2\rangle$ was printed erroneously instead of $\langle l_x^2\rangle$. As in the previous definition $\langle l^2\rangle = 3\langle l_x^2\rangle$ it follows that the correct value of $\langle l^2\rangle$ is 7.0 Å^2.

[17] T. Lyon and T. A. Litowitz, J. Appl. Phys. 27, 179 (1955).

TABLE III. Characteristic displacement of an average proton relative to the molecular center of gravity.

	Glycerol				*n*-propanol		
T°K	$\frac{1}{3}\langle r_i^2\rangle$ (Å^2)	$2D_p\tau_{00}$ (Å^2)	$\langle l_x^2\rangle$ (Å^2)	T°K	$\frac{1}{3}\langle r_i^2\rangle$ (Å^2)	$2D_p\tau_{00}$ (Å^2)	$\langle l_x^2\rangle$ (Å^2)
266	0.14	0.63	1.23	153	0.14		3.8
293	0.16	0.76	1.40	173	0.20		4.1
334	0.24	0.80	1.33	218	0.26		
369	0.28	0.60	1.20	233	0.28	0.27	3.8
403	0.32			263	0.30	0.30	3.9
453	0.40			293	0.38	0.37	4.7
Average or typical value	0.25	0.70	1.29	Average or typical value	0.25	0.31	4.1

of the thermal cloud set up by a proton round the diffusing center. The results for glycerol and *n*-propanol are given for comparison in Table III.

It is seen that the vibrational amplitude and the diffusive displacement by small steps of the molecular direction are of a similar magnitude, whereas the jump caused by a sudden change of molecular direction tends to be the dominant feature. In neither case is the motion of the center of gravity, vibratory or diffusive, important within the temperature ranges investigated.

It is important to notice that in both cases the value of $\langle r_i^2\rangle$ varies between about 0.5 and 1.2 Å^2 corresponding to root-mean-square radii of 0.7–1.1 Å. Such a large value of the rms radius is probably not associated with true vibrational motions. The internal proton vibrations are not exited at the low temperatures considered and the remaining zero-point vibration has a rms radius of an order of 0.1 Å. It seems therefore probable that $\langle r_i^2\rangle$ is also associated with a rotation but now around a long axis like the C-C-C line of the molecules considered. The fact that $\langle r_i^2\rangle$ varies with temperature could well be explained by a gradual onset of an increasing number of rotations as the temperature increases. Any alternative explanation to the large value of $\langle r_i^2\rangle$ would be that the molecule undergoes large and rapid shape changes much like the possible deformations of an elastic spring. Only a very careful linewidth study combined with studies of the inelastic scattered neutron spectrum can reveal these finer details of the molecular motion.

VII. A GENERALIZED WAY OF REPRESENTING LINEWIDTH DATA

As was shown in an earlier work,[18] the linewidth data for a given substance (hydrogenous liquid or solid) obtained at different temperatures and given as $\tau_{00}\Delta\omega$ versus the dimensionless variable $2``D"\tau_{00}\kappa^2$ seem to reduce to one single curve, a generalized linewidth representation.

It is easy to understand this representation of the data, if we remember that according to Eq. (5a) the linewidth in case of negligible self-diffusion is given by

$$\tau_{00}\Delta\omega=2[1+\tfrac{2}{3}D_p\tau_{00}\kappa^2-e^{-[(1/6)\langle r_i^2\rangle+(1/6)\langle l^2\rangle]\kappa^2}]. \quad (8a)$$

If the diffusive term $\frac{4}{3}D_p\tau_{00}\kappa^2$ is subtracted from the observed data given by $\tau_{00}\Delta\omega$, one obtains a variable $\tau_{00}\Delta\omega'$ which will then be dependent on $\frac{1}{6}(\langle l^2\rangle+\langle r_i^2\rangle)\kappa^2=\frac{1}{6}\langle\Delta r^2\rangle\kappa^2$. This representation of the data should be approximately the same for all similar hydrogenous substances.

In Fig. 7 the observed variable $\tau_{00}\Delta\omega'$ is plotted versus the similarly observed variable $2(``D"-\frac{2}{3}D_p)\tau_{00}\kappa^2=\langle\Delta r^2\rangle\kappa^2$ for *n*-propanol and glycerol. In the figure the average linewidth curve given by

$$\tau_{00}\Delta\omega'=\tau_{00}(\Delta\omega-\tfrac{4}{3}D_p\kappa^2)=2(1-e^{-(1/6)\langle\Delta r^2\rangle\kappa^2}) \quad (8b)$$

is also plotted as a solid line. The average values of $\langle r_i^2\rangle+\langle l^2\rangle$ were taken from Table III as 3.33 Å^2 for glycerol and 9.0 Å^2 for *n*-propanol.

For both liquids the general trend is the same and in agreement with the prediction. Unfortunately the de-

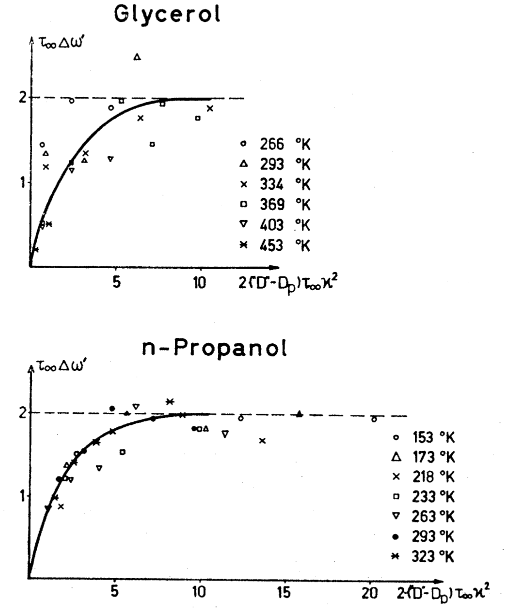

FIG. 7. The generalized plot of linewidth data obtained from quasi-elastic neutron scattering in glycerol and *n*-propanol. The solid line represents the calculated average linewidth curve.

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[18] K. E. Larsson, in *Proceedings of the Bombay Symposium on Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1965), Vol. II, p. 3.

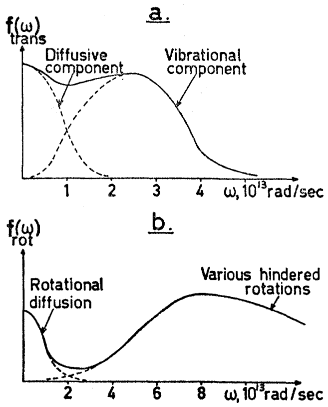

FIG. 8. Possible shapes of the frequency distribution for (a) hindered translations corresponding to the center-of-gravity motion and (b) hindered rotations corresponding to motions relative to the center of gravity.

rived data on glycerol are rather inaccurate but for *n*-propanol for which the term $\frac{4}{3}D_p\tau_{00}$ is smaller the agreement is very satisfactory. The two average curves differ only little from each other and therefore it is fair to speak about one general linewidth representation for both substances.

What has been plotted in Fig. 7 is nothing but the relative vibrational and rotational properties of the two liquids. The rotational diffusion characterized by the term $\frac{2}{3}D_p\kappa^2$ was subtracted from the observed linewidth data. An entirely identical result would have been obtained if diffusion of the center of gravity had occurred as described by Eq. (7a), only that now the term $(2D+\frac{4}{3}D_p)\kappa^2$ must be subtracted from the measured linewidth $\Delta\omega$. If the vibration of the center of gravity had been of importance a term containing $2W_e=\frac{1}{6}\langle r_e^2\rangle\kappa^2$ would have been included in the exponent of Eq. (8b). The conclusion is thus: If all diffusive processes by small steps, translational characterized by D or rotational characterized by D_p, are subtracted from the sum of processes resulting in linewidth broadening, the rest which is mainly connected with hindered rotations or diffusion in large steps is fairly temperature-insensitive and constant for a particular liquid. This is in contrast to the diffusive contributions from small steps which appear strongly temperature-dependent.

VIII. DISCUSSION

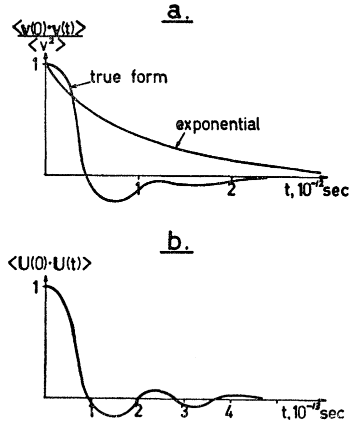

FIG. 9. Possible shapes for the self-correlation functions which form the basis for the frequency distributions of Fig. 8: (a) the velocity autocorrelation function corresponding to the center-of-gravity motion, (b) the angular autocorrelation function corresponding to the relative, hindered rotational motion.

Studies[1,2,4,5] on simple liquids have shown that the translational diffusive and the hindered translational (=vibratory) motions together form a generalized frequency distribution $f_{\text{trans}}(\omega)$ somewhat of the shape shown in Fig. 8(a). The corresponding velocity autocorrelation function[19–21] $\langle v(0)\cdot v(t)\rangle$ has consequently a form strongly deviating from the simple exponential $e^{-t/\tau}$ as shown in Fig. 9(a). The existence of collective motions in simple liquids was proved beyond doubt. There is no reason why molecules, i.e., their centers of gravity, should not participate in such collective motions of longitudinal as well as transversal nature.

As has been found in the present investigation the motions of rotational character seem to behave quite in the same way as the translational. Rotational diffusive motion occurring in small steps was shown to contribute to the line broadening as well as the larger steps, which may be identified as part of a type of hindered rotations. Earlier studies of hydrogenous substances have shown that inelastic neutron scattering of hindered rotational character occurs.[22–24] It is thus natural that the relative motion discussed in this paper, and which is all of rotational nature, shows a similar frequency distribution

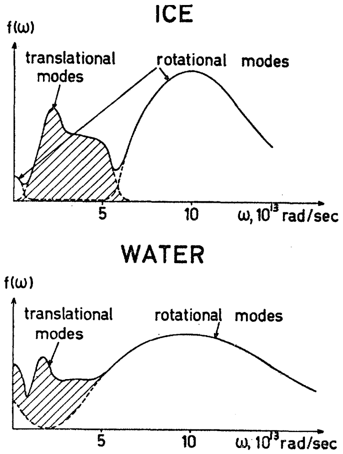

FIG. 10. Observed shapes of the frequency distributions in ice and water and the proposed division into a hindered translational and a hindered rotational component.

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[19] A. Rahman, K. S. Singwi, and A. Sjölander, Phys. Rev. **126** 986 (1962); **127**, 997 (1962).

[20] A. Rahman, Phys. Rev. **136**, A405 (1964).

[21] A. Rahman (private communication).

[22] B. N. Brockhouse, Nuovo Cimento Suppl. **9**, 45 (1958).

[23] D. J. Hughes, H. Palevsky, W. Kley, and E. Tunkelo, Phys. Rev. **119**, 872 (1960).

[24] K. E. Larsson and U. Dahlborg, J. Nucl. Energy **16**, 81 (1962).

$f_{\rm rot}(\omega)$, which could be of a type illustrated in Fig. 8(b). This would mean that the corresponding autocorrelation function $\langle \mathbf{U}(0)\cdot\mathbf{U}(t)\rangle$ for a unit vector **U** fixed to the molecule also is very strongly deviating from an exponential form for short times but rather is similar to the autocorrelation function for translational velocities as indicated in Fig. 9(b). There is also all reason to expect the hindered rotational motions to be of collective character.

The discussion carried out above gets support from slow-neutron-scattering observations on water and ice. As several investigations[24,25] have shown, a frequency distribution for ice and water may be obtained from the neutron data of the type shown in Fig. 10. The broad hindered rotation peak around $\omega\sim 10^{14}$ rad/sec$\sim$0.067 eV is somewhat broadened in going from ice to water. A smearing out of details in going from ice to water also occurs in the region below $\omega\sim 6.10^{13}$ rad/ sec or 0.045 eV corresponding to the energy range of hindered translations. The main change occurs in the diffusive region for $\omega<3\cdot 10^{12}$ rad/sec or about 2 meV. The rotational diffusive modes might in general exist in the solid as indicated in the ice spectrum of Fig. 10. The translational diffusive modes are observed only in the liquid phase and are taking over an increasing number of the available translational degrees of freedom as the temperature rises. The corresponding autocorrelation functions for the proton motion in water are consequently strongly nonexponential.

Recent neutron-scattering experiments[26] on acetic acid CH_3COOH and on trifluoroacetic acid CF_3COOH as well as on partially deuterated methyl alcohol CD_3OH and CH_3OD have clearly shown the importance of hindered rotational motions of the CH_3 group as well as of the motions of the OH group in forming a higher- and a lower-frequency range, respectively, in the generalized frequency distribution $f(\omega)$. Both of these liquids have such a low viscosity at 20°C (about 1 cP as in water discussed above) that the translational diffusion must be a dominant feature in producing the quasi-elastic peak. As discussed in Secs. III and IV above, a careful analysis of this peak would, however, probably reveal its dependence on rotational diffusion. It should be noted that the effect of rotational jumps is best seen when the viscosity is of the order of 1 P.

Using nuclear-magnetic-resonance methods for investigation of liquid dynamics, Hunt and Powles[27] in a recent investigation came to the conclusion that the main difficulty in understanding nuclear-magnetic-resonance data on liquids is that nothing is directly known about the correlation functions mentioned above. It has been customary to assume that the autocorrelations decay exponentially. The slow-neutron-scattering experiments have, however, shown beyond all doubt that the correlation functions are nonexponential. A simple exponential decay for $\langle \mathbf{v}(0)\cdot\mathbf{v}(t)\rangle$ would, for instance, lead to only simple diffusion modes of motion, which is not in agreement with any neutron-scattering results. The view of an exponentially decaying autocorrelation function often taken in various relaxation time experiments such as dielectric, ultrasonic, and nuclear-magnetic-resonance experiments should most probably be changed to one in which the fundamental correlations are nonexponential for shorter times. Probably most motions are collective in liquids as well as in solids.

In many cases of investigation of liquid dynamics by the nuclear-magnetic-resonance method the radio frequency of the apparatus is of the order of 10^7 cps, which is very small compared to $1/\tau_c$, where τ_c may be of the order of 10^{-11} sec (low-viscosity liquid). If now the slope of the frequency distribution $f(\omega)$ for small ω values ($\sim 10^7$ cps) is very nearly zero, it seems that the difference in using a true $f(\omega)$ shape in accordance with Figs. 8(a) and 8(b) or to use one with a simplified shape such as $\tau_c/(1+\omega^2\tau_c^2)$ will lead to similar results simply because in the long time limit, corresponding to small ω values, all methods should give a similar result determined by simple diffusion. It was thus shown[19] quite generally that $f_{\rm trans}(0)=2MD/\pi k_BT=(2/\pi)t_\beta$, where t_β is the inverse value of the friction coefficient in the Langevin diffusion equation. If, however, the value of τ_c for the investigated liquid is such that $\omega\tau_c\sim 1$ (very high viscosity), then the assumption of an exponential correlation function would definitely lead to an erroneous result for the interpretation of nuclear-magnetic-resonance relaxation times in microscopic terms.

In a recent series of papers by Gordon[28–30] on the interpretation of certain Raman and infrared spectra a view of the dynamical events in molecular liquids was developed which is in close agreement with the present discussion based on neutron-scattering results. The important agreement is that the rotational velocity autocorrelation functions show a strong deviation from exponential form at short times. Also the analysis of experimental results made by Gordon indicate that the large jump diffusion is equivalent to a free rotation over a limited angle. This is exactly what was assumed in the present work when describing the jump motion by a Gaussian with a width $\rho(t)$ varying as t^2. It thus seems that the same sort of information regarding the nature of the rotational diffusion may be derived from neutron-scattering data and from Raman and infrared light scattering and absorption experiments. The basic view of an exponentially decaying correlation function earlier taken in statistical mechanics is not correct for times of the order of 10^{-12} sec in low-viscosity liquids.

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IX. CONCLUSION

After a series of investigations of the quasi-elastic neutron spectra scattered from several hydrogenous liquids it has been possible to construct a model which seems to contain many of the important phenomenological features that are hidden in such spectra. It has been shown that the local fluctuations occuring near a selected molecule causes this molecule to move in a very complex way:

(a) A motion relative to the molecular center of gravity which may be supposed to consist of at least three components: (1) small and gradual directional changes of the molecular center line; (2) vibrations of the atoms superimposed on these small diffusive directional changes and possibly free or hindered rotations around the molecular symmetry line; (3) large directional changes of the molecular symmetry line which are probably quantized motions of the molecule in the field of its neighbors.

(b) A motion of the center of gravity of the molecule which might consist of: (1) vibratory motions; (2) diffusive motions. The complete picture of the molecular motion is a rotational translational diffusion of the molecule on which a vibrational motion is superimposed.

It is pointed out that probably the hindered rotational motion as well as the hindered translational has non-exponential velocity autocorrelation functions, which may well explain the results obtained from relaxation-time studies by nuclear-magnetic-resonance, dielectric, and ultrasonic methods, and replace the view of relaxation-time distributions or at least form an important complement to it.

It is shown that reasonable and plausible connections may be obtained between the mean lifetimes obtained from neutron-scattering experiments and the relaxation times obtained from dielectric and to some extent from ultrasonic studies of liquids.

It is found that the neutron-scattering results on rotational diffusion are in complete agreement with information extracted from Raman and infrared spectroscopy on liquids.

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