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Rotational Molecular Motion and the Transient Nature of Liquids as Seen by Slow-Neutron Scattering

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The analysis of neutron spectra scattered from molecular solids and liquids presents a formidable problem which so far has been only slightly touched upon. For a period of ten years, the translational motions of atoms in monatomic liquids have been investigated by neutron spectroscopists; their theoretical interpretation has reached a certain degree of refinement. An understanding of the effects of rotational motions on the neutron spectra scattered from molecular liquids, however, has not been developed to the same degree. The aim of the present work is to use some simple but reasonable model for the translational motions and to investigate in more detail the effect of the various possible rotational motions on the observed neutron spectrum. The general principle used is that translational and rotational motions are statistically uncorrelated. Thus, when the molecule as a whole vibrates and diffuses, it is assumed that it can also perform librations, free rotations, or rotational diffusion. Phonon expansions are done for the molecular vibrations and librations. Sears's basic theory is used to describe the free rotations and rotational diffusion. A cross section is obtained which contains all the basic components in the scattered-neutron spectrum. A discussion of "good"- and "bad"-resolution measurements is carried through. The value of older neutron-linewidth determinations is discussed. It is concluded that the resolution width ought to be $\leq 0.1\times$(the width of the rotational spectrum) if finer details of the rotational motion should be observed as resolved structure. With the aid of good-resolution data it is shown that the nature of the rotational motion changes drastically over the liquid range, from librations to almost free rotations. Comparison is made to changes of rotational motion of ions in the phase transition from the ferro- to the para-electric phase in the solid state. It is shown that from such observations of molecular motion the liquid appears as a phase transition or as a transient phenomenon.

I. INTRODUCTION

Neutron-scattering experiments have shown that single excitations (phonons) exist in a solid up to the melting point.[1,2] The lifetime of these phonons is of the order 10^{-12} sec, which means that the change in the microscopic atomic motions in passing the melting point is not too drastic.[3,4] The static long-range order is lost upon melting, but local order still exists for periods long enough to define a vibrational atomic motion which shows a memory of the collective behavior in the solid phase. As the temperature is gradually increased and the boiling point is approached, the liquid density decreases; even the local order becomes questionable in the gas phase above critical temperature.[5,6]

The question is to what degree does this transient nature of a liquid become evident through the study of molecular motions in the solid, liquid, and gas phases. Several experimental methods were used to investigate these questions in detail.[7] That slow neutrons offer a particularly powerful tool in the time range 10^{-13}–10^{-11} sec and the space range 0.1–10 Å is shown by the considerable number of papers published in the period 1960–68 dealing with slow-neutron-scattering studies on various hydrogenous liquids and solids.[8–10] At the beginning of this period a basic understanding of the observed neutron spectra was lacking. At the present time it is undoubtedly proved that if the proton motion in a complex hydrogenous substance is studied, not only the c.m. motion of the molecule is observed, but also the rotational motions, which often play a dominant role in the observed scattering picture.[11–19] This fact was not understood from the start of the neutron-scattering studies some 15 years ago. The first theoretical attempts to predict the neutron-scattering cross section concerned only the c.m. motion; the molecule was approximated by a point-like particle.[20–26] Such theories and models were quite correctly applied to scattering results on simple liquids like Ar and metals in liquid form. The application of these simple models to molecular liquids and solids like alcohols, hydrocarbons, water, glycerol, etc., now appears highly questionable. In the early studies no serious attempt was made to take relative molecular motions of a rotational or librational nature into account. Certain fundamental facts were, however, revealed.

On the short time scale for neutron observation the atomic motions in monatomic substances show considerable similarities in high-temperature solids and liquids. Diffusive motions in liquids occur mostly on a longer time scale, such that the simple asymptotic behavior predicted by Einstein, $\langle x^2 \rangle = 2Dt$, is not reached until a relaxation time τ has elapsed, during which vibrational motions develop. This is also true for molecular liquids consisting of nonspherical molecules. In simple liquids like Ar, and in the case of spherical molecules like methane, the asymptotic diffusive behavior is probably reached within 10^{-11} sec, or less, and therefore the effects of diffusion of the center of mass of the particle is clearly observed in these cases.[27–29] The typical features of slow-neutron spectra scattered from incoherent scatterers like hydrogenous substances are two regions of intensity: a near-elastic region, in which a rather narrow peak is observed, and an inelastic region, in which a broad spectrum with more or less pronounced structure is observed. Because the near-elastic region, corresponding to small energy transfers, is formed by energy exchange between the neutron and various diffusive modes of motion, it is quite clear that high resolution is required to learn about the true nature of diffusive motion of either a translational or rotational nature. Therefore, it is not surprising that conclusions drawn from the observations have undergone a gradual change as the resolution grew better and better with the development of new techniques and more intense neutron sources.

The classical example is the study of the full width at half-maximum of the quasielastic peak in hydrogenous liquids. From early water studies[30–35] it was concluded that the linewidth is *smaller* than that predicted by simple diffusion theory; this was taken as indicating that in between translational displacements leading to diffusion the water molecule vibrates to a certain extent as if in a solid. These experiments were performed with an ingoing neutron linewidth 0.2–2 meV. Soon after, it was found from cold-neutron studies with an ingoing neutron spectrum width of 2 meV that in liquids like glycerol, pentane, alcohols, etc., the linewidth is much *larger* than could be expected from diffusion theory.[36–39] This was taken as an indication that some other proton motion dominates the motion on the short time scale 10^{-13}–10^{-11} sec. Recent experiments[40] with relatively high resolution (ingoing linewidth ~ 0.1 meV) performed on pentane and pentanol lead to the conclusion that, in these liquids, the near-elastic scattering or quasielastic peak has two components: a narrow one close to the width expected from simple diffusion, and a broader one of order 0.5–1 meV. An experiment with ultrahigh resolution[41] on glycerol covering a very narrow energy range at a small momentum transfer has given a linewidth in possible agreement with the value expected from simple diffusion theory. Still later experiments,[42] with an ingoing neutron linewidth of 0.08 meV, greater statistical accuracy, and careful analysis of the effects of multiple scattering, have shown the same tendency, but the broadening of the sharp central peak is smaller than that predicted from diffusion theory for the c.m. motion and more like that predicted for a solid in which the vibrating molecules perform both librations and some type of damped rotational motion. Damping of the motions will lead to a lifetime broadening of the central peak. Diffusion broadening will be observed using ultrahigh resolution and for small momentum transfers even for larger molecules, although it will be small. In general, rotational behavior will thus dominate the scattering picture in the near-elastic region.

From these experiences in the near-elastic region, it is clear that the inelastic region will be dominated by the frequency distribution of the hindered translational modes of motion (c.m. vibration, phonons) and the various hindered rotational modes of motion (librations, damped rotations, free rotations). Such effects have been observed and discussed at considerable length in the literature.

The present work is an attempt to unite these ideas into one model which will lead to an experimentally useful cross section and may be directly compared with recent experiments. The model was formulated in an earlier work[12] and extended in a later one.[13] The basic framework used in this presentation is the same, but now the inelastic part of the cross section is included as a phonon expansion, an expansion of the librational part, and an expansion for the rotational part. To describe the rotational motion the general formulation developed by Sears[11] is used. The model is presented in Sec. II and the cross-section formulation in Secs. III and IV.

In order to understand the old and new experimental results it is of vital importance to investigate the effects of resolution on the observed neutron spectra. Therefore, the meaning with "good" and "bad" resolution is discussed at some length in Sec. V. It is shown that the old and new results are completely understood on the basis of the present cross-section formulation.

The main effort of the present work is to show to what extent the observed neutron spectra may change when the investigated sample passes from solid form to liquid form and further passes over the liquid range. In particular, the effects of various rotational forms of motion are investigated. In Sec. VI it will be shown that the effects of temperature variation on the molecular-rotational motions, in a very clear way, reveal the nature of the whole liquid phase.

II. MODEL

The basic model adopted here for the molecular motion has already been described in part.[12,13] It is assumed that the vibrational motions of the atoms in the molecule are not excited and contribute only a slowly varying Debye-Waller factor to the double differential cross section. The motions seen by the neutron are thus of rotational and translational nature. To make calculations possible it is assumed that there is no statistical correlation between rotations and translations. To simplify further, the molecules are assumed to move as rigid units. As will be seen later on it is fairly easy to relax this condition and allow for internal molecular librations or rotations of methyl groups, etc.

Many rather sophisticated models were created in the past to describe the translational motion of the center of mass of the molecule. In order to obtain a simple explicit form for the cross section it is assumed that the motion of the center of mass may either be simple diffusion for a time τ_1' or vibrations around a residence position for a time τ_0'.

Independent of these motions, the molecule is supposed to be able to perform a motion relative to its center of mass, namely, *either* librational motion for a time τ_0 during which its average angular orientation does not change, *or* rotational motion for a time τ_1 during which its angular orientation changes. The rotational motion may be a free rotation, a rotational diffusion, or more probably some intermediate case of friction damped rotation. To fix the ideas we shall consider only the two limiting cases, free rotation and rotational diffusion, respectively. The times τ_k and τ_k', with $k=0$ or 1, are average times; a time τ_k or τ_k' means t with a probability e^{-t/τ_k}, etc.

It should be remarked at this stage that the physical meaning of the various times can be stated as follows: If the frequency distribution of the velocity autocorrelation function $\langle \vec{v}(0)\vec{v}(t)\rangle$ is in general denoted by $f(\omega)$, then we may think of $f(\omega)$ as divided into two parts:

$$f(\omega)=\frac{\tau_0'}{\tau_0'+\tau_1'}\,f(\omega)_{\text{vib}}+\frac{\tau_1'}{\tau_0'+\tau_1'}\,f(\omega)_{\text{dif}}, \tag{1}$$

where the first part describes the vibrational part of the motion and the second part describes the diffusive part, respectively. The time ratios give the fraction of all modes of motion due to vibrations and due to diffusion. This principle is common to all models created during the last ten years and merely gives the correct limiting behaviors at short and long times. In a similar way one may imagine the rotational motions to be described by two equations of motion: one describing the librational motion during τ_0 and another describing the rotational motion during τ_1. Thus, the ratios τ_1'/τ_0' and τ_1/τ_0 give the division of molecular translational and rotational motion into (i) various types of diffusive motions in small or large steps and (ii) various motions of more or less damped periodic character.

The formulation of the translational motion of the center of mass, within the framework discussed here, was first developed by Singwi and Sjölander.[20] The method was later extended by the present author to cover the rotational motion and the resulting cross sections were applied to experimental data.[12,13] The doubly differential cross section per scattering nucleus has the following structure:

$$\frac{d^2\sigma}{d\Omega\, d\omega}=\frac{a^2}{2\pi}\,\frac{k}{k_0}\,\frac{e^{-\beta\omega}}{\tau_0'+\tau_1'}\left(\frac{\tau_0'A+\tau_1'B-2AB}{1-(AB/\tau_0'\tau_1')}+\text{c. c.}\right). \tag{2}$$

Here a is the incoherent scattering length, $\vec{k}$ and $\vec{k}_0$ the scattered and ingoing neutron wave vectors, $\hbar\vec{\kappa}=\hbar(\vec{k}-\vec{k}_0)$ the momentum transfer, $\hbar\omega$ the energy transfer in the scattering process and $\beta=\hbar/2k_B T$. We further have

$$A=\frac{1}{\tau_0+\tau_1}\,\frac{\tau_0 a_A+\tau_1 b_A-2a_A b_A}{1-(a_A b_A/\tau_0\tau_1)}\ , \tag{3a}$$

$$B=\frac{1}{\tau_0+\tau_1}\,\frac{\tau_0 a_B+\tau_1 b_B-2a_B b_B}{1-(a_B b_B/\tau_0\tau_1)}\ . \tag{3b}$$

The four quantities a_A, b_A, a_B, and b_B may be expressed in the intermediate scattering functions $\chi_T(\kappa,t)$ and $\chi_R(\kappa,t)$ for translational and rotational motion, respectively, in the following way:

$$a_A = \int_0^\infty dt \exp(-i\omega t - t/\tau_{00})\chi_T^0(\kappa, t)\chi_R^0(\kappa, t), \quad (4a)$$

$$b_A = \int_0^\infty dt \exp(-i\omega t - t/\tau_{10})\chi_T^0(\kappa, t)\chi_R^1(\kappa, t), \quad (4b)$$

$$a_B = \int_0^\infty dt \exp(-i\omega t - t/\tau_{01})\chi_T^1(\kappa, t)\chi_R^0(\kappa, t), \quad (4c)$$

$$b_B = \int_0^\infty dt \exp(-i\omega t - t/\tau_{11})\chi_T^1(\kappa, t)\chi_R^1(\kappa, t). \quad (4d)$$

Here we have $1/\tau_{kl} = 1/\tau_k + 1/\tau_l'$, with k and l equal to 0 or 1, respectively. The superscripts 0 to 1 on $\chi_T(\kappa, t)$ or $\chi_R(\kappa, t)$ refer to the time periods τ_0' or τ_0, and τ_1' or τ_1, respectively. It is seen that, if $\tau_1'=0$ and $\tau_0 \rightarrow \infty$, we have $a_B = b_B = B = 0$, corresponding to a solid. On the other hand, if $\tau_0'=0$ and $\tau_1' \rightarrow \infty$, we have $a_A = b_A = A = 0$, corresponding to the asymptotic diffusive behavior found in a liquid. Whether both τ_0' and τ_1' play a role in the observed cross section depends upon two factors: (i) The physical process observed must contain both phases of motion, (ii) the time scale of observation must be such that both phases of motion are observed.

In order to obtain the cross section in an explicit form the following forms are assumed for the intermediate scattering functions $\chi_T(\kappa, t)$ and $\chi_R(\kappa, t)$:

$$\chi_T^0(\kappa, t) = \exp\{-\kappa^2[\gamma(0)_T - \gamma(t)_T]\}, \quad (5)$$

where

$$\gamma(t) = (\hbar/2M)\int_0^\infty (\coth\beta\xi \cos\xi t + i\sin\xi t)[f(\xi)_T/\xi]d\xi, \quad (6)$$

and $\kappa^2\gamma(0) = 2W_T$ (the Debye-Waller factor for c. m. oscillations during τ_0'); M is the mass of the molecule. Equation (5) is expanded in the phonon expansion[43]

$$\chi_T^0(\kappa, t) = e^{-2W_T}\{1 + 2W_T[\gamma(t)_T/\gamma(0)_T] + \cdots\}. \quad (6')$$

During the time τ_1' we assume the simple diffusion expression

$$\chi_T^1(\kappa, t) = e^{-D\kappa^2 t}, \quad (7)$$

where D is the self-diffusion coefficient for the c. m. motion.

In order to describe the motions relative to the center of mass, which are of rotational nature, different forms are assumed to cover the periods τ_0 and τ_1. The librational motion during τ_0, when the molecule performs rotational oscillations around an equilibrium direction, has been considered in some detail by various authors[16-19]. We take for the intermediate scattering function during τ_0 the following approximate expression:

$$\chi_R^0(\kappa, t) = \exp\{-\kappa^2[\gamma(0)_R - \gamma(t)_R]\}, \quad (8)$$

where

$$\gamma(t)_R = (\hbar/2M_R)\int_0^\infty (\coth\beta\xi \cos\xi t + i\sin\xi t)f(\xi)_R/\xi \, d\xi, \quad (9)$$

an expression analogous to (6) but with rotational mass M_R replacing molecular mass M. $f(\xi)_R$ is the frequency distribution of rotational oscillations; $\kappa^2\gamma(0)_R = 2W_R$ is the Debye-Waller factor for the rotational oscillations. Explicit expressions for the effective rotational mass M_R have been discussed for linear[18] and other molecules.[19] In the case of linear molecules, we have

$$M_R = I\kappa^2\left(\sum_{l=1}^\infty l(l+1)(2l+1)j_l(\kappa r)^2\right)^{-1} \xrightarrow[\kappa r \ll 1]{} \frac{3I}{2r^2}, \quad (10)$$

where I is the moment of inertia of the molecule, $j_l(\kappa r)$ is a spherical Bessel function of order l, and r is the distance of the scattering nucleus from the center of mass of the molecule. An expansion of (8) gives

$$\chi_R^0(\kappa, t) = e^{-2W_R}\{1 + 2W_R[\gamma(t)_R/\gamma(0)_R] + \cdots\}. \quad (8')$$

The rotational motion during τ_1, when the molecule changes its direction in space, is described by the general formalism developed by Sears,[11] which is valid if there is no statistical correlation between rotational and translational motions and if the isotropic forces acting on a molecule are much stronger than the anisotropic ones. We have

$$\chi_R^1(\kappa, t) = \sum_{l=0}^\infty (2l+1)j_l(\kappa r)^2 F_l(t), \quad (11a)$$

where $F_l(t)$ is a rotational relaxation function. In this formulation the mechansim of the rotational motion is hidden in the functions $F_l(t)$. Explicit forms for $F_l(t)$ are given for the limiting cases (i) free rotation and (ii) rotational diffusion. In general, $F_l(t)$ has the form

$$F_l(t) = F_{1l} + F_{2l}(t), \quad (11b)$$

where F_{1l} is the asymptotic value of $F_l(t)$ as t tends to long times, and $F_{2l}(t)$ describes the time behavior of $F_l(t)$ for shorter times. For free rotation F_{1l} often has a finite value, whereas for damped rotation such as rotational diffusion, $F_{1l}=0$. The actual forms of $F_l(t)$ for spherical and linear molecules are[14] (free rotation)

$$F_l(t) = \frac{1}{2l+1}\left(1 + 2\sum_{\mu=1}^{l}(1 - \mu^2 t^{*2})e^{-\mu^2 t^{*2}/2}\right) \quad (11c)$$

for spherical, and

$$F_l(t) = \frac{1}{\pi}\frac{\Gamma(\frac{1}{2}(l+1))}{(\frac{1}{2}l)!}E_l + \frac{2}{\pi}\sum_{n=1}^{l}\frac{\Gamma(\frac{1}{2}(l-n+1))\,\Gamma(\frac{1}{2}(l+n+1))}{[\frac{1}{2}(l-n)]!\,[\frac{1}{2}(l+n)]!} \times \exp(-\tfrac{1}{2}n^2t^{*2})M(-\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}n^2t^{*2}) \quad (11d)$$

for linear molecules. Here $t^* = t(k_BT/I)^{1/2}$, $M(a,b,x)$ is Krummer's confluent hypergeometric function, and $E_l = 0$ and 1 for l odd and even, respectively. As seen from these expressions, the constant terms F_{1l} in $F_l(t)$, combined with the Bessel functions, lead according to (11) to functions $F(\kappa r)$, which are

$$F(\kappa r) = \sum_{l=0}^{\infty} j_l(\kappa r)^2 = \frac{\mathrm{Si}\, 2\kappa r}{2\kappa r} \tag{11e}$$

for spherical molecules, and

$$F(\kappa r) = \frac{1}{\pi} \sum_{l=0}^{\infty} (2l+1) j_l(\kappa r)^2 \, \frac{\Gamma(\frac{1}{2}(l+1))}{(\frac{1}{2}l)\,!} \, E_l \tag{11f}$$

for linear molecules.

For the case of rotational diffusion, when the rotational autocorrelation function obeys a simple diffusion equation, the form of $F_l(t)$ is

$$F_l(t) = e^{-l(l+1)D_r t}, \tag{12}$$

where D_r is a rotational diffusion constant. It is seen that $F_l(t)$ according to (12) does not show the correct short-time behavior because the time expansions of (12) are linear functions of time. For long times, the form (12) should be acceptable. For short times, the behavior predicted by the free-rotation expressions like (11c) and (11d) should be correct. A better representation than either of (11c), (11d), or (12) would be a combination of both. This problem will be discussed in some detail later. It may be noticed that the situation in describing the rotational motions has its complete analogy in the description of the translational motions of the center of mass: The short-time behavior of the width $\gamma(t)$ of the Gaussian self-correlation function should be $(vt)^2$ and is not correctly given by a simple diffusion form, which is linear in time. In the following the two alternatives for $F_l(t)$ given by free rotation and rotational diffusion, respectively, will be considered separately to describe the intermediate scattering function $\chi_R^1(\kappa, t)$ valid for the period τ_1. The characteristic feature of the proposed model is that the molecule is supposed to perform rotational oscillations around an equilibrium direction for a certain time τ_0, while changing its spatial orientation by some type of rotational motion during τ_1. One could imagine another combination in which the molecule performs rotational diffusion during τ_0 and changes its spatial orientation by free rotation during τ_1. Such an assumption would seem probable from a consideration of the observed form of $F_1(t)$ and $F_2(t)$ for a simple molecular liquid like methane. However, the variation of quasielastically scattered neutron intensity with κ, predicted by such an assumption, is not in agreement with observation, as will be shown in Sec. IV.

In Eq. (2) and in the results reported in Sec. III the cross section is given per scattering nucleus (mostly protons). Should the molecule contain several incoherently scattering nuclei at the same or at different distances from the center of mass, a summation over all the scatterers in the molecule should be made to obtain the cross section per molecule. Such a sum consists of terms of the type given by Eq. (2).

III. SCATTERING CROSS SECTION FOR "IDEAL" SOLID AND LIQUID STATES

Calculation of the cross section by use of Eqs. (2)–(12) is straightforward but cumbersome. Only two simplified cases will be formulated in this paper, namely, the case A $\tau_0' \gg \tau_1'$, corresponding to a solid, and the case B $\tau_1' \gg \tau_0'$, corresponding to a liquid without any vibratory component of the molecular c. m. motion. The neutron scattering from slowly moving molecules of nonspherical type like propane, pentane, the corresponding alcohols, etc., in solid as well as liquid form, is probably well described by the first case. The second case is approached although rarely fully seen by present day neutron-scattering experiments on lighter spherical molecules, like methane in liquid form.

A. $\tau_0' \gg \tau_1'$

The conditions for observation of this case are, that either the sample is in a solid state, or the observation time is so short that asymptotic diffusive motion of the center of mass is not reached. The cross section per scattering nucleus (proton) is given by the simplified form [cf. Eqs. (2) and (3)]

$$\frac{d^2\sigma}{d\Omega\, d\omega} = \frac{a^2}{2\pi} \frac{k}{k_0} \, e^{-\beta\omega}(A + \mathrm{c.c.}). \tag{13}$$

The two constituents of A, a_A, and b_A are given as follows:

$$a_A = e^{-2W_T - 2W_R} \int_0^{\infty} dt\, e^{-i\omega t - t/\tau_{00}} [1 + \kappa^2 \gamma(t)_T + \cdots] \times [1 + \kappa^2\gamma(t)_R + \cdots] \; . \tag{14}$$

Higher phonon terms are not included in the expansions because they do not add to the physical clarity of the resulting formulas. It is seen that a_A will contain two terms which are foldings of the Lorentz function $(1/\tau_{00}^2 + \omega^2)^{-1}$ and one-phonon terms. As discussed in the Appendix the real part of these integrals is much greater than the imaginary part, which is therefore neglected. The final value of a_A is

$$a_A = \tau_{00} e^{-2W_T - 2W_R} \Bigg(\frac{1}{1 + i\omega\tau_{00}}$$

$$+ e^{\beta\omega} \frac{\hbar\kappa^2}{2M_R} \int_{-\infty}^{+\infty} \frac{f(\xi)_R}{\xi} \, \frac{1}{e^{(2\beta\xi)} - 1} \, \frac{\tau_{00}\, d\xi}{1 + (\omega + \xi)^2 \tau_{00}^2}$$

$$+e^{\beta\omega}\frac{\hbar\kappa^2}{2M}\int_{-\infty}^{+\infty}\frac{f(\xi)_T}{\xi}\,\frac{1}{e^{(2\beta\xi)}-1}\,\frac{\tau_{00}\,d\xi}{1+(\omega+\xi)^2\tau_0^2}$$

$$+\kappa^4\int_0^\infty\frac{dt}{\tau_{00}}\;e^{-i\omega t-t/\tau_{00}}\gamma(t)_T\,\gamma(t)_R+\cdots\Big)\,. \qquad (15)$$

Similarly, one finds for b_A

$$b_A=e^{-2W_T}\int_{-\infty}^{+\infty}dt\exp(-i\omega t-t/\tau_{10})\left[1+\kappa^2\gamma(t)_T\right]$$

$$\times\sum_{l=0}^{\infty}(2l+1)j_l(\kappa r)^2\left[F_{1l}+F_{2l}(t)\right]\;. \qquad (16)$$

The rotational intermediate scattering function expressed as the sum over l is written in a form which is valid both for free rotation and for rotational diffusion. For free rotation, the terms F_{1l} have in general finite values, and for rotational diffusion $F_{1l}=0$ for all values of l. The expression for b_A can be approximately written as

$$b_A=\tau_{10}e^{2W_T}\left(\frac{F(\kappa r)}{1+i\omega\tau_{10}}+\sum_{l=1}^{\infty}(2l+1)j_l(\kappa r)^2\int_0^\infty\frac{dt}{\tau_{10}}\exp(-i\omega t-t/\tau_{10})F_{2l}(t)+e^{\beta\omega}\frac{\hbar\kappa^2}{2M}F(\kappa r)\right.$$

$$\left.\times\int_{-\infty}^{+\infty}\frac{f(\xi)_T}{\xi}\,\frac{1}{e^{2\beta\xi}-1}\,\frac{\tau_{10}d\xi}{1+(\omega+\xi)^2\tau_{10}^2}+\kappa^4\sum_{l=1}^{\infty}(2l+1)j_l(\kappa r)^2\int_0^\infty\frac{dt}{\tau_{10}}\exp(-i\omega t-t/\tau_{10})\gamma(t)_TF_{2l}(t)+\cdots\right), \qquad (17)$$

where

$$F(\kappa r)=\sum_{l=0}^{\infty}(2l+1)j_l(\kappa r)^2F_{1l}\,.$$

Examples of possible forms of $F(\kappa r)$ for free rotation was given in Eqs. (11e) and (11f). For rotational diffusion, $F_{10}=1$ and all other F_{1l}'s equal 0, so that $F(\kappa r)=j_0(\kappa r)^2$ for this case. The forms of $F_{2l}(t)$ for free rotation of spherical and linear molecules are given by the second terms of Eq. (11c) and (11d). For rotational diffusion, $F_{2l}(t)=F_l(t)$ is given by Eq. (12).

With these definitions and with the assumptions, more fully elaborated in the Appendix, that (i) the real part of the folding integrals defined in a_A and b_A are much greater than the imaginary parts, and (ii) that $\omega^2\tau_{00}\tau_{10}\gg 1$ in the inelastic scattering region, the cross section is after some manipulation given by

$$\frac{d^2\sigma}{d\Omega d\omega}=\frac{a^2}{\pi}\,\frac{k}{k_0}\,\frac{e^{-2W_T-\beta\omega}}{\tau_{00}+\tau_{10}}\left[\frac{ab+c\omega^2}{b^2+d\omega^2+e\omega^4}+\tau_{10}\sum_{l=1}^{\infty}(2l+1)j_l(\kappa r)^2\,\mathrm{Re}\left(\int_0^\infty\frac{dt}{\tau_{10}}\exp(-i\omega t-t/\tau_{10})F_{2l}(t)\right)\right.$$

$$+\tau_{00}e^{-2W_R+\beta\omega}\frac{\hbar\kappa^2}{2M_R}\int_{-\infty}^{+\infty}\frac{f(\xi)_R}{\xi}\,\frac{1}{e^{2\beta\xi}-1}\,\frac{\tau_{00}d\xi}{1+(\omega+\xi)^2\tau_{00}^2}+\frac{\hbar\kappa^2}{2M}e^{\beta\omega}\left(\tau_{00}e^{-2W_R}\int_{-\infty}^{+\infty}\frac{f(\xi)_T}{\xi}\,\frac{1}{e^{2\beta\xi}-1}\,\frac{\tau_{00}d\xi}{1+(\omega+\xi)^2\tau_{00}^2}\right.$$

$$\left.\left.+\tau_{10}F(\kappa r)\int_{-\infty}^{+\infty}\frac{f(\xi)_{\mathrm{T}}}{\xi}\,\frac{1}{e^{2\beta\xi}-1}\,\frac{\tau_{10}d\xi}{1+(\omega+\xi)^2\tau_{10}^2}\right)+\cdots\right]. \qquad (18)$$

Here we have

$$a=\tau_{00}^2e^{-2W_R}+\tau_{10}^2F(\kappa r)-2\tau_{00}\tau_{10}F(\kappa r)e^{-2W_R-2W_T},$$

$$b=1-F(\kappa r)e^{-4W_T-2W_R}\;,$$

$$c=\tau_{00}^2\tau_{10}^2\left[e^{-2W_R}+F(\kappa r)+F(\kappa r)e^{-2W_R-2W_T}\right]\,,$$

$$d=\tau_{00}^2+\tau_{10}^2+2\tau_{00}\tau_{10}F(\kappa r)e^{-4W_T-2W_R}\;,$$

$$e=\tau_{00}^2\,\tau_{10}^2\;.$$

In order to simplify the expression and bring out the basic physics, the folding terms in a_A and b_A are not included in Eq. (18). These terms as well as higher phonon terms in the expansions given by Eqs. (5′) and (8′) may easily be included in the cross section.

As will be seen from Eq. (18), the cross section predicts a quasielastic peak of non-Lorentzian shape and an inelastic part determined by three components: the rotational term due to the molecular motion occurring during τ_1, the librational term due to the molecular motion during τ_0, and finally the c.m. vibration due to a molecular motion continuing all the time. This last term is dominated by the frequency distribution $f(\xi)_T$ and reduces to the usual one-phonon term, if the width τ_{00}^{-1} or τ_{01}^{-1} of the Lorentz functions $(1/\tau_{00}^2+\omega^2)^{-1}$ or

$(1/\tau_{01}^2+\omega^2)^{-1}$, respectively, are small compared to the width of $f(\xi)_T$. This is the case if a well-defined and narrow quasielastic peak is observed. In such a case the last term may be approximated by the expression

$$e^{-2W_T}\,\frac{\hbar\kappa^2}{2M}\,\frac{\tau_{00}e^{-2W_R}+\tau_{10}F(\kappa r)}{\tau_{00}+\tau_{10}}\,\frac{f(\omega)_T e^{-\beta\omega}}{\omega\sinh\beta\omega}\,, \tag{19}$$

which is just the one-phonon term multiplied with a κ-dependent factor caused by the librations and the rotations, respectively. To the same degree of approximation, the librational term in Eq. (18) reduces to the librational "one-phonon" term

$$e^{-2W_T}\,\frac{\hbar\kappa^2}{2M_R}\,\frac{\tau_{00}}{\tau_{00}+\tau_{10}}\,\frac{f(\omega)_R e^{-\beta\omega}}{\omega\sin\beta\omega}\,. \tag{20}$$

The rotational term is simple for the case of rotational diffusion, when $F_{2l}(t)=F_l(t)=e^{-l(l+1)D_r t}$, namely,

$$\frac{\tau_{10}e^{-2W_T-\beta\omega}}{\tau_{00}+\tau_{10}}\sum_{l=1}^{\infty}\frac{(2l+1)j_l(\kappa r)^2[1+D_r l(l+1)\tau_{10}]}{[1+D_r l(l+1)\tau_{10}]^2+\omega^2\tau_{10}^2}\,. \tag{21}$$

When the rotation is free the form of the rotational term depends upon the molecular shape. For spherical molecules the rotational term is

$$\frac{e^{-2W_T-\beta\omega}}{\tau_{00}+\tau_{10}}\,\frac{4}{\sqrt{\pi}}\sum_{l=1}^{\infty}j_l(\kappa r)^2\sum_{m=1}^{l}\left(\frac{I}{2m^2k_BT}\right)^{3/2}\int_{-\infty}^{+\infty}\omega'^2\exp-\left(\frac{I(\omega')^2}{2m^2k_BT}\right)\frac{\tau_{10}\,d\omega'}{1+(\omega'-\omega)^2\tau_{10}^2}\,, \tag{22a}$$

and for linear molecules

$$\frac{e^{-2W_T-\beta\omega}}{\tau_{00}+\tau_{10}}\,\frac{1}{\pi}\sum_{l=1}^{\infty}(2l+1)j_l(\kappa r)^2\sum_{m}^{l}{}'\,\frac{\Gamma(\frac{1}{2}(l-m+1)\,\Gamma(\frac{1}{2}(l+m+1))}{[\frac{1}{2}(l-m)]!\,[\frac{1}{2}(l+m)]!}\int_{-\infty}^{+\infty}\frac{I}{m^2k_BT}|\omega'|\exp\left(-\frac{I(\omega')^2}{2m^2k_BT}\right)\frac{\tau_{10}\,d\omega'}{1+(\omega'-\omega)^2\tau_{10}^2}\,. \tag{22b}$$

The prime over the second summation means sum over all odd m's, when l is odd, and over all even m's (starting with 2), when l is even. It is seen that the rotational term changes shape from a sum of Lorentzian functions for the small step rotational diffusion, Eq. (21), to a sum of Maxwellian-shaped curves for free rotation [Eqs. (22a) and (22b)]. If the rotational motion is strongly damped, which occurs if $\tau_1<(I/k_BT)^{1/2}$, it is seen from the foldings in Eqs. (22a) and (22b), that the shape of the rotational cross section becomes intermediate between Lorentzian- and Maxwellian-like.

In order to see the nature of the quasielastic peak, it is instructive to consider two limiting cases: either that the librations dominate, $\tau_0\gg\tau_1$, or that the rotations dominate, $\tau_1\gg\tau_0$. In these limits the quasielastic peak reduces to

$$\left(\frac{d^2\sigma}{d\Omega\,d\omega}\right)_{\mathrm{q.el}}=\frac{a^2}{\pi}\,\frac{k}{k_0}\,\tau_{00}e^{-2W_T-2W_R-\beta\omega}\times\frac{1-F(\kappa r)e^{-2W_T-2W_R}}{[1-F(\kappa r)e^{-2W_T-2W_R}]^2+\omega^2\tau_{00}}\,, \tag{23}$$

if $\tau_0\gg\tau_1$ and reduces to a similar expression with τ_{00} replaced by τ_{10}, if $\tau_1\gg\tau_0$. This cross section is of Lorentzian shape, and the full width at half-maximum (FWHM) is defined by

$$\Delta\omega=\frac{2}{\tau_{00}}\left[1-F(\kappa r)e^{-2W_T-2W_R}\right], \tag{24}$$

for $\tau_0\gg\tau_1$, and a similar expression with τ_{00} replaced by τ_{10} if $\tau_1\gg\tau_0$. The limiting behavior at small and large κ values is

$$\Delta\omega\xrightarrow[\kappa\to 0]{}\frac{\langle r_T^2\rangle+\langle r_R^2\rangle+2r^2}{3\tau_{00}}\,\kappa^2\,, \tag{24$'$}$$

$$\Delta\omega\xrightarrow[\kappa(\text{large})]{}\frac{2}{\tau_{00}}\,, \tag{24$''$}$$

where $\langle r_T^2\rangle$ and $\langle r_R^2\rangle$ are the mean square radii of vibration and of libration, respectively. The line broadening is a lifetime effect that disappears, if τ_{00} and $\tau_{10}\to\infty$.

A useful quantity, which may be tested experimentally, is the angular variation of the intensity of the quasielastic peak. The ω integration of the quasielastic peak according to Eq. (18) may be carried out in closed form and is given by

$$I(\kappa)_{\mathrm{q.el}}=a^2\,\frac{\tau_{00}e^{-2W_R}+\tau_{10}F(\kappa r)}{\tau_{00}+\tau_{10}}\,e^{-2W_T}\,. \tag{25}$$

This formula predicts that, if the libration is dominating, the intensity is given by

$$I(\kappa)_{\mathrm{q.el}}=a^2\,e^{-2W_T-2W_R}\,, \tag{26}$$

whereas, if the rotation is dominating, it is given by

$$I(\kappa)_{\mathrm{q.el}}=a^2\,F(\kappa r)\,e^{-2W_T}\,. \tag{27}$$

As the variation of $I(\kappa)$ is quite different in the two cases these formulas can be tested experimentally without difficulty.

The angular variation of the rotational inelastic spectrum is also easily obtained by performing the ω integration of the rotational term in Eq. (18). The result is

$$I(\kappa)_{\mathrm{rot}}=\frac{a^2\,\tau_{10}\,e^{-2W_T}}{\tau_{00}+\tau_{10}}\,[1-F(\kappa r)]\ . \tag{28}$$

This result may be useful, if the rotational spectrum is rather narrow, occuring close to the quasielastic peak.

B. $\tau_1'\gg\tau_0'$

This is the limiting liquid case when the c.m. motion is governed by simple diffusion. The cross section per molecule simplifies to

$$\frac{d^2\sigma}{d\Omega\,d\omega}=\frac{a^2}{\pi}\,\frac{k}{k_0}\,e^{-\beta\omega}\,(B+\mathrm{c.c.})\ . \tag{29}$$

The term B is constructed of a_B and b_B, which are given by

$$a_B=e^{-2W_R}\int_0^\infty dt\,\exp(-i\omega t-t/\tau_{01}-D\kappa^2 t)$$

$$\times\,[1+\kappa^2\gamma(t)_R+\cdots]\ , \tag{30}$$

and

$$b_B=\sum_{l=0}^{\infty}[(2l+1)j_l(\kappa r)^2$$

$$\times\int_0^\infty dt\,\exp(-i\omega t-t/\tau_{11}-D\kappa^2 t)F_l(t)]\ . \tag{31}$$

These expressions are quite analogous to Eqs. (14) and (16), respectively, the difference being that the intermediate scattering function for the c.m. motion $\chi_T(\kappa,t)$ is changed to the form given by Eq. (7). By a treatment analogous to the one just described for the solid, the cross section is found to be

$$\frac{d^2\sigma}{d\Omega\,d\omega}=\frac{a^2}{\pi}\,\frac{k}{k_0}\,\frac{e^{-\beta\omega}}{\tau_{01}+\tau_{11}}\left[\frac{ab+c\omega^2}{b^2+d\omega^2+e\omega^4}+\tau_{11}\sum_{l=1}^{\infty}(2l+1)j_l(\kappa r)^2\,\mathrm{Re}\left(\int_0^\infty\frac{dt}{\tau_{11}}\exp(-i\omega t-t/\tau_{11}-D\kappa^2 t)F_{2l}(t)\right)\right.$$

$$\left.+\tau_{01}\,e^{-2W_R+\beta\omega}\,\frac{\hbar\kappa^2}{2M_R}\int_{-\infty}^{+\infty}\frac{f(\xi)_R}{\xi}\,\frac{1}{e^{2\beta\xi}-1}\,\frac{\tau_{01}\,d\xi}{(1+D\kappa^2\tau_{01})^2+(\omega+\xi)^2\tau_{01}^2}+\cdots\right]\ . \tag{32}$$

Here we have

$$a=\tau_{01}^2\,(1+D\kappa^2\tau_{11})\,e^{-2W_R}+\tau_{11}(1+D\kappa^2\tau_{01})F(\kappa r)$$

$$-\,2\tau_{01}\tau_{11}F(\kappa r)\,e^{-2W_R}\ ,$$

$$b=(1+D\kappa^2\tau_{01})(1+D\kappa^2\tau_{11})-F(\kappa r)e^{-2W_R}\ ,$$

$$c=\tau_{01}^2\tau_{11}^2[(1+D\kappa^2\tau_{01})e^{-2W_R}+(1+D\kappa^2\tau_{11})F(\kappa r)$$

$$+\,2F(\kappa r)\,e^{-2W_R}]\ ,$$

$$d=(1+D\kappa^2\tau_{01})^2\tau_{11}^2+(1+D\kappa^2\tau_{11})^2\tau_{01}^2$$

$$+\,2\tau_{01}\tau_{11}F(\kappa r)\,e^{-2W_R}\ ,$$

$$e=\tau_{01}^2\tau_{11}^2\ .$$

As will be seen from this expression, the cross section is quite similar to the expression found in case A, Eq. (18): a quasielastic peak of non-Lorentzian shape and an inelastic spectrum, this time dominated by only two terms, the rotational spectrum and the librational spectrum. In the present case the diffusion broadening of the ingoing neutron spectrum affects all terms.

The properties of the quasielastic peak are analogous to the previous case. If, again, the limiting forms for $\tau_0\gg\tau_1$ and $\tau_1\gg\tau_0$ are considered, one finds for the quasielastic peak the following Lorentzian shape:

$$\left(\frac{d^2\sigma}{d\Omega\,d\omega}\right)_{\mathrm{q.el}}=\frac{a^2}{\pi}\,\frac{k}{k_0}\,\tau_{01}\,e^{-2W_R-\beta\omega}$$

$$\times\frac{1+D\kappa^2\tau_{01}-F(\kappa r)\,e^{-2W_R}}{[1+D\kappa^2\tau_{01}-F(\kappa r)\,e^{-2W_R}]^2+\omega^2\tau_{01}}\ , \tag{33}$$

if $\tau_0\gg\tau_1$, and a similar expression with τ_{01} replaced by τ_{11}, if $\tau_1\gg\tau_0$. The FWHM is now determined by

$$\Delta\omega=(2/\tau_{01})[1+D\kappa^2\tau_{01}-F(\kappa r)\,e^{-2W_R}]\ , \tag{34}$$

if $\tau_0\gg\tau_1$, and a similar expression with τ_{01} replaced by τ_{11}, if $\tau_1\gg\tau_0$. The FWHM is a complicated expression, using the full Eq. (32), but the limiting behaviors for small and large κ values are simpler:

$$\Delta\omega\xrightarrow[\kappa\to 0]{}2\left(D+\frac{\langle r_R^2\rangle+2r^2}{6\tau_{01}}\right)\kappa^2\ , \tag{35}$$

$$\Delta\omega\xrightarrow[\kappa\ (\mathrm{large})]{}2\left(\frac{1}{\tau_{01}}+D\kappa^2\right)\quad\text{if }\tau_0\gg\tau_1 \tag{36}$$

and τ_{11} replacing τ_{01}, if $\tau_1\gg\tau_0$. It is found that Eqs. (35) and (36) are of exactly the form that was predicted in an earlier work [compare Eqs. (35b) and (35c) in Ref. 12]. The area under the quasielastic peak is given by

$$I(\kappa)_{\text{q.el}} = a^2 \frac{\tau_{01} e^{-2W_R} + \tau_{11} F(\kappa r)}{\tau_{01} + \tau_{11}} \tag{37}$$

The area under the rotational term is

$$I(\kappa)_{\text{rot}} = a^2 \frac{\tau_{11}}{\tau_{01} + \tau_{11}} [1 - F(\kappa r)]. \tag{38}$$

The inelastic terms are in the present case (liquid) similar to the corresponding terms in the previous case (solid) with the following obvious changes: The Debye-Waller factor e^{-2W_T} is missing, in Eq. (21) the factor $1 + D_r l(l+1)\tau_{10}$ is changed to $1 + D\kappa^2\tau_{11} + D_r l(l+1)\tau_{11}$, in Eqs. (22a) and (22b) the factor $1 + (\omega' - \omega)^2\tau_{10}^2$ is changed to $(1 + D\kappa^2\tau_{11})^2 + (\omega' - \omega)^2\tau_{11}^2$, finally τ_{00} is changed to τ_{01}, and τ_{10} to τ_{11}. With these changes Eqs. (21), (22a), and (22b) are still valid.

C. Internal Molecular Rotations

In the treatment given thus far, the molecule was supposed to be rigid. In real molecules internal librational or rotational motions may occur. A typical example is the motion of a methyl group in many organic molecules. This motion may, for instance, be a libration or a free rotation. Such an internal motion may be included within the theoretical framework developed in a previous work.[12] In such a case, the motion relative to the center of mass has two components: (i) the motion of the molecule considered as rigid just treated above and (ii) the motion of a part of the molecule in a system participating in both rotation of the rigid molecule and in translational motion. The calculations are very lengthy but straightforward. If the internal librations and rotations are treated in exactly the same way as was described above for the over-all rotation of the rigid molecule, the resulting cross sections are found to contain expected new features: (i) If the internal motion is a librational motion, a new Debye-Waller factor e^{-2W_i} describing the effect of the square of the librational amplitude enters as well as a librational inelastic spectrum governed by the frequency distribution $f(\omega)_i$ of the librational-angular-velocity autocorrelation function; or (ii) if the internal motion is a free rotation, a new factor $F(\kappa b)_i$ analogous to the function $F(\kappa r)$, discussed in connection with Eqs. (11d), (11e), (17), (18), and (32), will enter as well as a rotational spectrum appearing in the inelastic region. b is the distance from the considered proton to an axis of rotation fixed in the molecule. This rotational spectrum is quite similar to the one discussed above in connection with Eq. (11). If the moving unit is a methyl group, its frequency of oscillation will be high due to its small moment of inertia, and the inelastic contribution will occur for energy transfers considerably larger than the contribution due to rigid-molecule rotations or librations. This was in fact verified experimentally by several research groups.[44, 45]

The cross section is too complicated to be discussed in detail in the present paper. As the area of the quasielastic peak is a useful experimental quantity, we will state here the final expression for this area for internal librational motion and for solid state:

$$I(\kappa)_{\text{q.el}} = a^2 \frac{\tau_{00} e^{-2W_R} + \tau_{10} F(\kappa r)}{\tau_{00} + \tau_{10}} e^{-2W_T - 2W_i}, \tag{39}$$

and for internal free rotation, solid state,

$$I(\kappa)_{\text{q.el}} = a^2 \frac{\tau_{00} e^{-2W_R} + \tau_{10} F(\kappa r)}{\tau_{00} + \tau_{10}} F(\kappa b)_i e^{-2W_T}. \tag{40}$$

If instead we consider a simple diffusive liquid, the Debye-Waller factor e^{-2W_T} disappears and the τ's are changed from τ_{00} and τ_{10} to τ_{01} and τ_{11}, respectively. The width of the quasielastic peak will now contain the new factor $2W_i$ in addition to the previous factor $2W_T$. These are the main effects; secondary effects are numerous and will not be considered here.

IV. MIXTURE OF STATES OF MOLECULAR MOTION IN A LIQUID

As shown in Eq. (2) the true dynamical situation in a liquid probably is a mixture of the molecular motions during the periods τ_0' and τ_1'. Evaluation of the cross section according to Eq. (2) is, however, extremely complex and the chance of obtaining a result of some physical transparency is small. One way to approximate the true situation is to consider the motion of the molecules as a simple mixture of the extreme cases occurring when either $\tau_0' \gg \tau_1'$ or $\tau_1' \gg \tau_0'$. This gives a simplified form for the cross section:

$$\frac{d^2\sigma}{d\Omega\, d\omega} = \frac{a^2}{\pi} \frac{k}{k_0} e^{-\beta\omega} \left(\frac{\tau_0'}{\tau_0' + \tau_1'} A + \frac{\tau_1'}{\tau_0' + \tau_1'} B + \text{c.c.} \right). \tag{41}$$

In such a description of the cross section the transition terms between the two phases of motion are not considered. The cross section appears as a sum of the cross sections for the solid and simple diffusion cases. Such a model is probably useful only for bad resolution measurements to be discussed below. Furthermore, the validity of this simplified model is questionable unless the observation time and range is long enough (low-energy neutrons, small angle of observation) and the physical process is such that both phases of motion are really well developed.

This idea may be clarified if we assume a Gaussian form of $G_s(r, t) \sim e^{-r^2/4\rho(t)^2}$ and remember the prediction of the uncertainty relation $\Delta p \, \Delta x \geq \hbar$, which gives $\Delta x \geq 1/\kappa$ if $\Delta p = \hbar\kappa$. The observation range is thus inversely proportional to $\kappa \simeq 2k_0 \times \sin\frac{1}{2}\theta$ for near-elastic scattering, where θ is the scattering angle. If the neutron velocity is v, the observation time δt is of order $\Delta x/v \geq 1/v\kappa$. Therefore, we have $\delta t \sim \hbar/E_0 \sin\frac{1}{2}\theta$. The observation range and time both increase as the ingoing neutron energy and scattering angle is decreased. The form of $\rho(t)$ for noble-gas liquids and for light spherical molecules is such that the asymptotic diffusive behavior $\rho(t) \to Dt$ is quickly reached. For heavier nonspherical molecules and probably for liquid metals, there exists a fairly long transition region in which $\rho(t)$ shows a smaller slope and may be said to behave as in a solid. For very much longer observation time or lower frequency in the analyzing probe (NMR, ESR, dielectric-relaxation-time studies), asymptotic diffusive behavior is the completely dominating feature unless the investigated substance has a very slow relaxation behavior as in glass.

A more realistic description of the c.m. motion of the molecules in a liquid could be obtained by using a better approximation for the intermediate scattering function $\chi_T^1(\kappa, t)$ than $e^{-D\kappa^2 t}$. Several models were proposed for this motion.[23–26] It was also clearly shown by neutron-scattering studies on simple liquids that diffusive as well as vibrational components must be included in a true description of atomic motions.[3–6,46] When, however, the neutrons are scattered from heavy nonspherical molecules, it is probable that the time scale of molecular motion is so long that only the vibrational part is actually observed, whereas the asymptotic diffusive linear-time behavior of the width function $\rho(t) \to Dt$ is never reached within the available interaction time between neutron and nucleus in the scattering molecule. It seems, therefore, probable that the present model for $\tau_0' \gg \tau_1'$ (solid state) should relatively well describe the scattering situation in such cases. For the lightest spherical molecules the diffusive behavior is probably observed. For such a case (like liquid methane) a more realistic description of $\chi_T(\kappa, t)$ is almost certainly necessary to describe the observed neutron-scattering result.

Another theoretical difficulty with the present simplified model concerns the rotational motion. The molecule is supposed to change its angular direction either by free rotation or by rotational diffusion. Most likely, components of both these modes of rotational motion exist in a real liquid. The experimentally studied rotational relaxation functions $F_l(t)$ contain components of both kinds.[47,48] It is an easy matter to modify the present model in such a way that both these rotational motions occur during τ_1 by assuming that during a time $f\tau_1$ the molecule rotates freely, and that during $(1-f)\tau_1$ it performs rotational diffusion (Fig. 1). This procedure, however, introduces another parameter f determined so that $0 < f < 1$. Therefore, this way out of the theoretical difficulty was not tried in the treatment given above.

One may argue that during the time τ_0 the molecule should be allowed to perform rotational oscillations superimposed on a rotational diffusion, and during τ_1 it should be allowed to rotate freely. This model was tried in an earlier work.[13] Such an assumption, however, leads to certain predictions which are not in agreement with observation. According to this model, the area of the quasielastic peak becomes

$$I(\kappa)_{\text{q.el}} = a^2 \frac{\tau_{00} j_0(\kappa r)^2 e^{-2W_R} + \tau_{10} F(\kappa r)}{\tau_{00} + \tau_{10}} e^{-2W_T - 2W_i} \tag{42}$$

for the case of a solid including the effect of internal molecular librations. The characteristic feature of this formula is that when $\kappa \to 0$ it may be expanded to give as a leading factor $I(\kappa)_{\text{q.el}} \sim 1 - \frac{1}{3}\kappa^2 r^2$ because r^2, being of order several Å^2, is supposed to be much larger than $\langle r_R^2 \rangle$, $\langle r_T^2 \rangle$, or $\langle r_i^2 \rangle$, which should all be smaller than 1 Å^2. The experimentally observed functions $I(\kappa)_{\text{q.el}}$ do not vary so rapidly with κ^2, at least not for lower temperatures, as will be shown in Sec. VI. The only way open to obtain a realistic form of $F_l(t)$ would therefore be to assume both rotational diffusion and free rotation to occur during τ_1. Such an assumption leads to an expression for the area of the quasielastic peak (solid state):

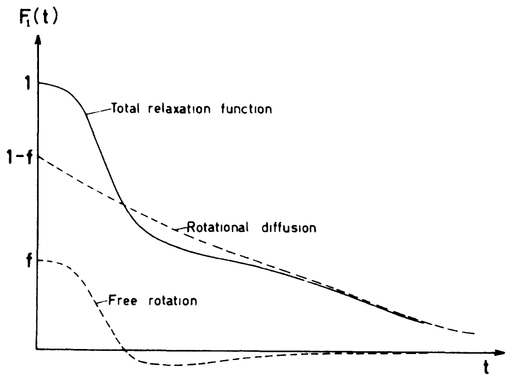

FIG. 1. Rotational relaxation function for $l = 1$ as composed of two components: free rotation during $f\tau_1$ and rotational diffusion during $(1-f)\tau_1$; linear molecule is assumed.

$$I(\kappa)_{\text{q.el}} = a^2 \frac{\tau_{00} e^{-2W_R} + \tau_{10}[fF(\kappa r) + (1-f) j_0(\kappa r)^2]}{\tau_{00} + \tau_{10}} \times e^{-2W_T - 2W_t} . \quad (43)$$

The difference between this result for the differential cross section and the previous one [Eq. (39)] is so small that it can probably not be observed. Also, other consequences of such an assumption differ so little from the cases when either free rotation or rotational diffusion are the only processes occurring during τ_1, that they would not be observed experimentally. From the present analysis one therefore arrives at the conclusion that it is very difficult to separate between the effects of the two kinds of rotational motion even by high-resolution neutron spectroscopy, at least for molecules more complex than, for example, methane.

V. GOOD- AND BAD-RESOLUTION MEASUREMENTS

The cross sections derived in Sec. III involve the basic idea that during the time τ_0 the molecule performs librations around a fixed direction, and during τ_1 it may either rotate freely or perform rotational diffusion. From an experimental point of view, it is of interest to examine more closely the actual shape of the near-elastic scattering.

The near-elastic scattering is characterized by a sharp central peak, the width of which is either determined by a lifetime effect (solid state) or by a combination of a lifetime effect and the c.m. diffusion (liquid state). The rotational motion produces in both cases an inelastic contribution, which may be concentrated quite close to the sharper quasielastic peak, as seen on energy scale, time-of-flight scale, or angular scale. For free rotation as well as for rotational diffusion, the corresponding inelastic-scattering term consists of a series of terms beginning with $l = 1$. If we fix our attention to this first term, we find for free rotation and linear molecule

$$\frac{\tau_1}{\tau_0 + \tau_1} \frac{3 j_1(\kappa r)^2 e^{-2W_T}}{\pi} \int_{-\infty}^{+\infty} \frac{I|\xi|}{2k_B T} e^{-I\xi^2/2k_B T} \times \frac{\tau_1 \, d\xi}{1 + (\xi - \omega)^2 \tau_1^2} , \quad (44)$$

and for rotational diffusion, we find

$$\frac{\tau_1}{\tau_0 + \tau_1} \frac{3 j_1(\kappa r)^2 e^{-2W_T}}{\pi} \frac{(1 + 2D_r \tau_1) \tau_1}{(1 + 2D_r \tau_1)^2 + \omega^2 \tau_1^2} . \quad (45)$$

If the central peak is narrow, it may be approximated with a δ function and the integral in Eq. (44) is directly carried out. It is then seen that Eq. (44) describes a Maxwellian-type distribution on each side of $\omega = 0$, the separation of the maxima being $2\Omega = 2(k_B T/I)^{1/2}$. Equation (45) describes a Lorentzian distribution of width $\Delta\omega = 2(1/\tau_1 + 2D_r)$. For molecules of the type like n-pentane and propane one finds the moment of inertia to be of the order 10^{-38} cm^2 g. Therefore, Ω is of the order 10^{12} sec^{-1} if T is about 250 °K. On the other hand, the rotational diffusion constant[11] D_r should be of the order 0.5×10^{12} sec^{-1}. It is thus found that the separation 2Ω of the maxima of Eq. (44) and the full width $\Delta\omega$ of the Lorentz function in Eq. (45) are of the same order, namely,

$$2\Omega = 2(k_B T/I)^{1/2} \sim 2 \times 10^{12} \text{ sec}^{-1} , \quad (46a)$$

$$\Delta\omega = 2(1/\tau_1 + 2D_r) \sim 2 \times 10^{12} \text{ sec}^{-1} . \quad (46b)$$

Here it was assumed that τ_1 is at least one order of magnitude larger than D_r^{-1}. If τ_1 were of the same order as D_r^{-1} or Ω^{-1}, the quasielastic peak would be determined by the relative magnitude of τ_0 and τ_1. If $\tau_0 \gg \tau_1$, the width of the quasielastic peak would be determined by τ_0^{-1}, and the broader rotational inelastic spectrum would not be observed because its area is determined by the ratio τ_1/τ_0. If $\tau_1 \gtrsim \tau_0$, the width of the quasielastic peak would be of the order $1/\tau_1$ ($\sim \Omega$ or D_r), and therefore it would be so wide that it could not be separated from the broader inelastic rotational spectrum. In fact, measurements indicate that τ_1 in molecular liquids like propane, n-pentane, propanol, pentanol, etc., may be of the order 10^{-11} sec. If τ_0 as well as τ_1 were of the order 10^{-12} sec, it would be impossible to separate a sharp quasielastic peak from the inelastic rotational spectrum, regardless of whether the rotation is free or diffusive. The principle of the discussion is illustrated in Fig. 2. The importance of good resolution in experiments aiming at a study of the rotational effects is obvious. The estimated width of the inelastic rotational spectra is, say, of the order 10^{12} sec^{-1} or about 1 meV and the width of the central quasielastic peak of the order 10^{11} sec^{-1} or about 0.1 meV. If the width of the ingoing neutron spectrum is of the order 1 meV, the two components are not separated. Only one broadened peak is observed, whose width is determined by a weighted sum of the narrow quasielastic peak and the broader inelastic rotational spectra (cf. Fig. 2).

It is quite clear from the analysis presented here that the linewidth studies carried out in various neutron observations have different meanings. Only in the limit of small values of κ do the observations with good and bad resolution give the same result. As seen from Eqs. (25) and (28), (37) and (38), the area under the inelastic rotational spectrum in the limit of small values of κ tends to $\tau_1/(\tau_0 + \tau_1) \frac{1}{3} \kappa^2 r^2$, whereas the area of the quasielastic peak tends to 1. Thus, if $\kappa r < 1$, the effect of the broader inelastic part is negligible compared to the central peak, and the width derived

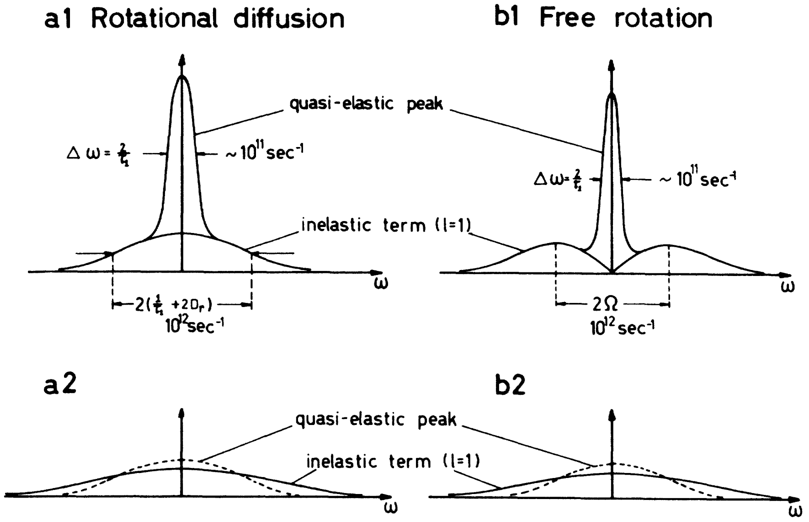

FIG. 2. Quasi-elastic peak and first rotational term ($l = 1$) as seen with good (a1 and b1) and bad (a2 and b2) resolution.

from the two series of observations leads to the same limit

$$\Delta\omega = 2\left(D + \frac{\langle r_R^2\rangle + 2r^2}{6(\tau_0 + \tau_1)}\right)\kappa^2 \quad \text{as } \kappa \to 0 \tag{47}$$

valid for the liquid and a similar form given by Eq. (24a) for the solid. If either of τ_0 or τ_1 is very long, we obtain $\Delta\omega = 2D\kappa^2$ for the liquid and $\Delta\omega = 0$ for the solid.

If we consider the limit of large values of κ it is instructive to include only the term $l = 1$ in the expansion of the rotational inelastic term. It is easily seen that the limiting value of the width is determined by the inelastic term as the area of the quasi-elastic peak tends to zero as κ increases. The limiting value of the width in the case of rotational

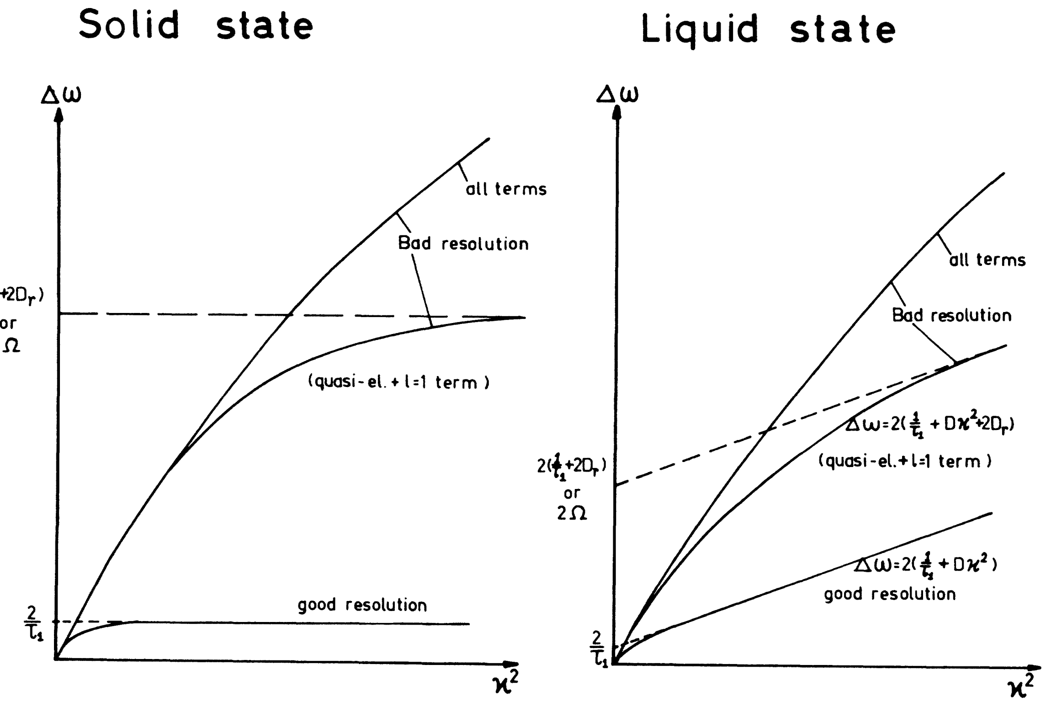

FIG. 3. Predicted behavior of the FWHM of the near-elastic scattering for good and bad resolution and for the case $\tau'_0 \gg \tau'_1$ (solid) and $\tau'_1 \gg \tau'_0 \gg \tau'_0$ (liquid). The oscillatory behavior of $\Delta\omega$ due to the spherical Bessel functions is smeared out by the presence of many protons at different distances from the center of mass in the molecule.

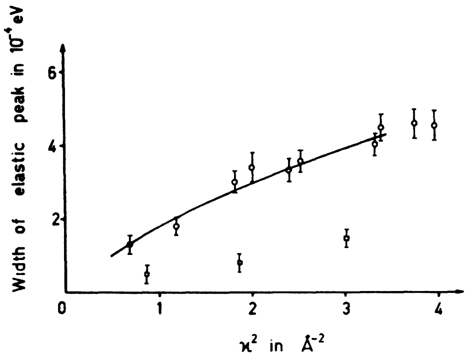

FIG. 4. Width of quasi-elastic peak in liquid pentane at -125 °C measured with bad resolution (solid line and circles) and good resolution (squares). Width of ingoing spectrum 2 meV for bad resolution and 0.1 meV for good resolution.

diffusion is

$$\Delta\omega = 2(1/\tau + D_r + D\kappa^2) \quad \text{as } \kappa \rightarrow \infty \tag{48a}$$

and approximately

$$\Delta\omega \simeq 2(\Omega + D\kappa^2) \quad \text{as } \kappa \rightarrow \infty \tag{48b}$$

for free rotation. In a solid, we have $D = 0$ and, correspondingly, τ_0 may be very long; therefore, no broadening is observed in such a case. For very bad resolution, terms with $l \geq 2$ may influence the values given in Eqs. (48a) and (48b). The predicted variation of linewidth as a function of κ^2 is shown in Figure 3.

A typical example of bad resolution is when the full beryllium-filtered cold-neutron spectrum is used as an ingoing spectrum. The width of this spectrum is of the order 2 meV at 5 meV. From Fig. 3 it it is seen that observations with such a broad ingoing spectrum on hydrogenous samples, which show a value of $\hbar D_r$ or $\hbar\Omega$ of the order 1 meV, would give a linewidth value ranging from $\Delta\omega \sim 2D_r$ or 2Ω, up to any larger value determined by the number of terms in the series expansion ($l \geq 2$) incorporated within the resolution width. This explains at once why, in many earlier studies on hydrogenous liquids, the linewidth curves show a saturation value of the order of 1 meV; not only the sharp quasielastic peak but also the first rotational term ($l = 1$) is included in the apparent quasielastic peak in such studies (cf. Fig. 7 of Ref. 13, and earlier references quoted in connection with it). Even several measurements with semimonochromatizing choppers giving ingoing energy widths of 0.5–0.8 meV in the cold-neutron range are to be classed as bad-resolution studies. To ensure good resolution, an ingoing neutron linewidth of about $0.1 \times 2D_r$ or $0.1 \times 2\Omega$ is necessary. In the examples discussed above this means a width of ≤ 0.1 meV. If measurements with good and bad resolution are compared, the observed linewidth results support the present predictions of Fig. 3 very strongly, as shown in Fig. 4, where experimental results on n-pentane are shown.[40]

Considering the conclusions drawn above regarding bad-resolution measurements, the question arises as to the validity of the results of older quasielastic neutron-linewidth data. In several cases of strongly hydrogen-bonded liquids like glycerol and n-propanol, the molecules are probably not free to rotate and possible orientational changes are rotational jumps. In such a case the bad-resolution studies probably give a reasonable result because the free-rotation term, according to Eq. (44), degenerates into a distribution whose width is defined approximately by $l^2/3\tau$, where $l = r\Omega\tau_1$, which is an average rotational jump. Also, the limiting value as $\kappa \rightarrow 0$ is correctly given by the bad-resolution data as $D_{\text{c.m.}} + D_{\text{rel}}$. The exact numerical values of some of the constants derived from bad-resolution data may, however, be in error.

VI. TRANSIENT NATURE OF A LIQUID

It was pointed our earlier that, if the rotational molecular motions change their nature over the liquid range, it will be observed if the area of the quasielastic peak is studied as a function of scattering angle (or equivalently, as a function of κ) at a set of representative temperatures covering the liquid range. This is illustrated by Eqs. (25), (37), (39), (40), and (43). If in the solid state $\tau_0 \gg \tau_1$ the quasielastic intensity is governed by a Debye-Waller factor $e^{-2W_R-2W_T-2W_i}$, one may, in general, guess that a similar situation is prevailing in the liquid state near the melting point. The relative values of τ_0 and τ_1 in a liquid must depend upon the shape of the molecules and the nature of the intermolecular forces. It is to be expected that $\tau_1 < \tau_0$ for long molecules sensitive to anisotropic forces or for strongly bound molecules, that $\tau_1 \sim \tau_0$ for molecules of intermediate length or more loosely bound molecules, and that $\tau_1 > \tau_0$ for spherical molecules or weakly bound molecules. If $\tau_1 \gg \tau_0$, which should be the prevailing situation in a dilute gas, the intensity [area $I(\kappa)$ under gas-model cross section] will be governed by $F(\kappa r)$. If $\ln I(\kappa)$ is plotted as a function of κ^2 assuming a case described by Eq. (37)

$$I(\kappa) = a^2 \frac{\tau_0 e^{-2W_R} + \tau_1 F(\kappa r)}{\tau_0 + \tau_1},$$

a set of curves as given in Fig. 5 is obtained when the ratio τ_0/τ_1 is varied between the limits 0 and ∞. It is also assumed that $2W_R = u^2\kappa^2$, with $u^2 = 0.4$ Å^2 and $r = 2.6$ Å. In order to bring out the principles

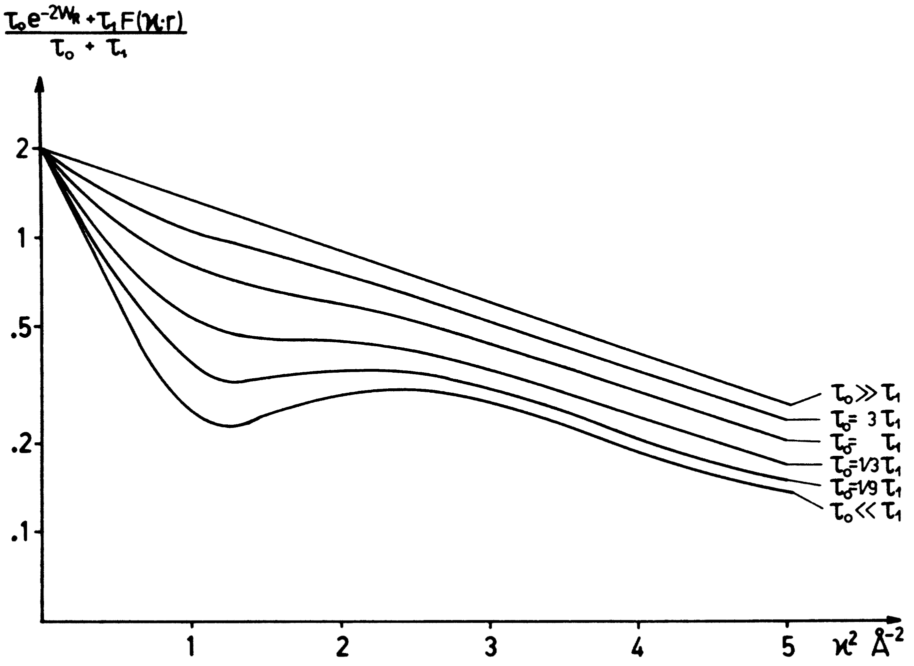

FIG. 5. Integrated intensity $I(\kappa)$ under the quasi-elastic peak as a function of κ^2 for various ratios τ_0/τ_1. Libration is supposed to occur during τ_0 and free rotation during τ_1.

clearly, it is assumed that only one distance r of the scattering nucleus from the molecular center of mass exists. In a real hydrogeneous molecule like pentane several values of r are involved, which means that the marked structure in $I(\kappa)$ will get lost upon summation of several terms, one for each proton. The general tendency of $I(\kappa)$ will, however, remain. The slope of the curves $I(\kappa)$ of Fig. 5 at the origin is obtained from a series expansion of Eq. (37):

$$I(\kappa)_{\mathrm{q.el}} = a^2 \left(1 - \frac{\tau_0 u^2 + \tau_1 \frac{1}{3} r^2}{\tau_0 + \tau_1} \kappa^2\right) \quad \text{as } \kappa \to 0. \qquad (49)$$

The slope varies from $-u^2$, if $\tau_0 \gg \tau_1$ to $-\frac{1}{3}r^2$, if $\tau_1 \gg \tau_0$. If τ_0 and τ_1 interchange their role over the liquid range, a characteristic variation of this slope as a function of temperature is expected. Such a variation has indeed been observed in neutron-scattering experiments on several liquids investigated, as shown in Fig. 6. Its magnitude varies from 0.1–0.3 Å^2, expected for librations in the solid state or just above the melting point in the liquid phase, to about 1.2–1.5 Å^2, corresponding to values of $r \sim 2$ Å near the boiling point. 1.5–2.5 Å corresponds typically to half the molecular length in the cases given in Fig. 6. The physical meaning of these observations is clear: Near melting point the investigated molecules perform librations; the amplitude of these librations increases steadily over the whole liquid range; and near the boiling point the molecules have a great probability to rotate freely. The rotational motion thus demonstrates the transient nature of the liquid.

To connect the preceding with the discussion at the beginning of this paper, one may state the physical implication of the data of Fig. 6 in a different way: If the generalized frequency distribution for rotational motions consists of two parts, one due to Langevin type of rotational diffusion with weight $\tau_1/(\tau_0 + \tau_1)$ and another due to damped oscillations (librations) with weight $\tau_0/(\tau_0 + \tau_1)$, the latter will dominate near the melting point, where-

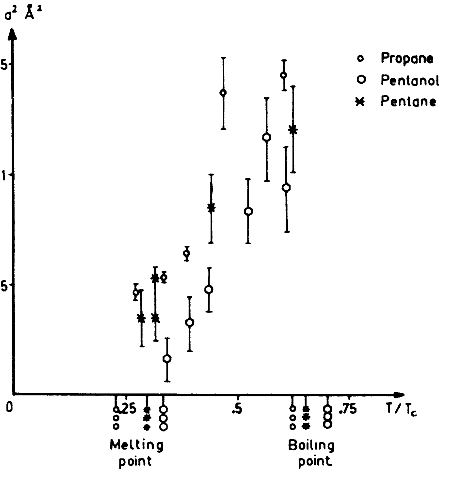

FIG. 6. Variation of the slope of $I(\kappa)$ for small κ values as a function of T/T_c for the temperature range between melting and boiling points of propane, pentane, and pentanol. T_c is the critical temperature. (After unpublished measurements of B. Friberg.)

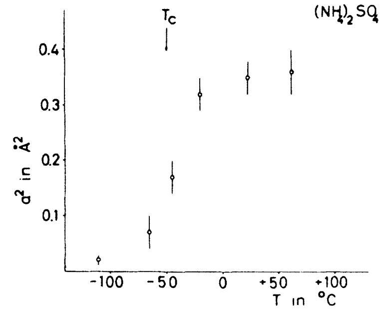

FIG. 7. Variation of the mean square amplitude of the oscillations of protons in ammonium sulphate around the ferroelectric transition point at − 50 °C (cf. Ref. 49).

as the former will dominate near the boiling point. The similarity between the dynamics of rotational and translational motions is striking. All the models and attempts to create a basic theory for the dynamics of translational motions of atoms in simple liquids during the last decade have indeed contained the two ingredients discussed above.

The same principle may be used to study a phase transition in a molecular solid such as the ferroelectric-paraelectric transition. A neutron-scattering study of the elastic and near-elastic intensity scattered from ammonium sulphate $(NH_4)_2SO_4$ was performed[49] at temperatures around the transition temperature − 50 °C. It is of particular interest in this connection to study the slope of the curves of $\ln I(\kappa)$ vs κ^2 for small κ values according to Eq. (49). The variation of the intensity of the elastic peak is completely dominated by the motion of NH_4 group. It is found that this slope varies from very small values of about 0.04 Å^2 below the transition point to values of about 0.37 Å^2 above the transition point (Fig. 7). The NH_4 ion is thus bound and performs librations in the ferroelectric phase, whereas it performs damped rotations in the paraelectric phase. The last conclusion may be drawn from the fact that the N-H distance is 1.05 Å, which is very near the value $(3\times 0.37)^{1/2}$ Å obtained for the value of r according to Eq. (49), if 0.37 is identified with $\frac{1}{3}r^2$. The similarity between the well-defined ferroelectric phase transition occurring over a temperature range of about 20 °C and the transition from the melting point to the boiling point in a liquid, is striking. The rapid change of dynamics in a transition in the solid is replaced by a slow and gradual change over the whole liquid phase. The liquid phase appears as one single-phase transition or as a transient phenomenon between the ordered solid phase and the disordered gas phase. A study of the rotational motions of molecules thus offers an elegant tool to demonstrate and evaluate the nature of the liquid phase. In the present discussion we have concentrated the interest to a narrow range of the neutron-scattering results, the quasielastic region. A phase change may cause a considerable change in the inelastic region as well, which is seen from Sec. III. Such results are well-known experimentally and are discussed in the literature.

VII. CONCLUSION

The present formulation of scattering cross sections is very general and allows various models for the molecular translational c.m. motion as well as for the rotational motion to be tested against experimental facts. In this paper, only two simple models are used for the hindered translations in order to bring out the main ideas clearly. Similarly, the rotational motion is assumed to be either a rotational diffusion or a free rotation. In spite of these apparent oversimplifications it is believed that the main features of several scattering experiments may be understood on the basis of the formulas presented. In fact, the present analysis together with some recent high-resolution neutron-scattering studies on molecular substances has shown that measurements with ingoing neutron spectra much wider than 10% of the first rotational term ($l = 1$) are only of limited usefulness. Bad-resolution data may give only a rough idea of the details of the molecular dynamics.

In cases when the damping of the rotational motion is not weak, the free rotations degenerate into a fraction of a free rotation or a rotational jump. For such a case the basic formalism for the rotational motion used in this paper [Eq. (11)] may break down. Empirical treatments of the observations are then the only possibilities of interpretation at present. An example of an experimental determination of the damping of rotations is given in Ref. 49. The part unknown to physics for the case of strong damping may be said to be concerned with the process occurring during the short time τ_1. The question of coupling between rotational and translational motions probably plays an important role in such cases.

APPENDIX

In connection with Eqs. (14), (16), (30), and (31) certain folding integrals have to be evaluated. In this Appendix we shall discuss only the integrals in Eqs. (30) and (31); the integrals in Eqs. (14) and (16) are treated analogously. We consider the integral

$$\int_0^\infty dt\, \gamma(t)_R \exp(-i\omega t - t/\tau_{01} - D\kappa^2 t). \tag{A1}$$

The integral to evaluate is

$$I=\int_0^\infty dt\, e^{-i\omega t-t/\tau_{01}-D\kappa^2 t}\int_0^\infty \frac{f(\xi)}{\xi}(\coth\beta\xi\cos\xi t+i\sin\xi t)\,d\xi$$

$$=\frac{1}{2}\int_0^\infty \frac{f(\xi)}{\xi}d\xi\int_0^\infty[\coth(\beta\xi)\,(e^{i\xi t}+e^{-i\xi t})+(e^{i\xi t}-e^{-i\xi t})]e^{-i\omega t-t/\tau_{01}-D\kappa^2 t}\,dt$$

$$=\frac{\tau_{01}}{2}\int_0^\infty \frac{f(\xi)}{\xi}d\xi\left[(\coth\beta\xi+1)\frac{1}{1+D_e\kappa^2\tau_{01}+i(\omega-\xi)\tau_{01}}+(\coth\beta\xi-1)\frac{1}{1+D\kappa^2\tau_{01}+i(\omega+\xi)\tau_{01}}\right]$$

$$=\int_0^{-\infty}\frac{f(-\xi)\,d(-\xi)}{-\xi}\,\frac{-1}{e^{2\beta\xi}-1}\,\frac{\tau_{01}}{1+D\kappa^2\tau_{01}+i(\omega+\xi)\tau_{01}}+\int_0^\infty\frac{f(\xi)}{\xi}d\xi\,\frac{1}{e^{2\beta\xi}-1}\,\frac{\tau_{01}}{1+D\kappa^2\tau_{01}+i(\omega+\xi)\tau_{01}}$$

$$=\tau_{01}\int_{-\infty}^{+\infty}\frac{f(\xi)}{\xi}d\xi\,\frac{1}{e^{2\beta\xi}-1}\,\frac{1+D\kappa^2\tau_{01}-i(\omega+\xi)\tau_{01}}{(1+D\kappa^2\tau_{01})^2+(\omega+\xi)^2\tau_{01}^2}=I_0+iI_1. \tag{A2}$$

Here we have

$$I_0=(1+D\kappa^2\tau_{01})\times\int_{-\infty}^{+\infty}\frac{f(\xi)}{\xi}\,\frac{1}{e^{2\beta\xi}-1}\,\frac{\tau_{01}\,d\xi}{(1+D\kappa^2\tau_{01})^2+(\omega+\xi)^2\tau_{01}^2} \tag{A3}$$

and

$$I_1=-\int_{-\infty}^{+\infty}\frac{f(\xi)}{\xi}\,\frac{1}{e^{2\beta\xi}-1}\,\frac{(\omega+\xi)\,\tau_{01}\,d\xi}{(1+D\kappa^2\tau_{01})^2+(\omega+\xi)^2\tau_{01}^2}\,. \tag{A4}$$

It is seen that if the width of the Lorentz function in I_0 and I_1 is small compared with the width of $f(\xi)$, and if $f(\xi)$ does not vary too rapidly within a range of ξ values corresponding to the width of the Lorentz function, we find $I_1 \ll I_0$ and we may in a first approximation neglect the imaginary part of I.

A further condition for obtaining the simple cross-section forms given in Eqs. (18) and (32) is that $\omega^2\tau_{00}\tau_{10}\gg 1$ and $\omega^2\tau_{01}\tau_{11}\gg 1$ in the inelastic region. A closer inspection of the full cross-section form of the quasielastic peak according to Eqs. (18) and (32) shows that its width $\Delta\omega$ is proportional to $(\tau_{00}\tau_{10})^{-1/2}$ or $(\tau_{01}\tau_{11})^{-1/2}$, respectively. In the inelastic region we have $\omega\gg\Delta\omega$ by definition. Therefore, the conditions $\omega^2\tau_{00}\tau_{10}\gg 1$ or $\omega^2\tau_{01}\tau_{11}\gg 1$ are automatically fulfilled in the inelastic region.

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Motion of the Center of Mass of Atoms and Molecules*

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The motion of the center of mass of atoms and molecules is described in the presence of external fields. In the case of electromagnetic radiation whose wavelength is much larger than the atom or molecule, we find that there will be a very small change in the component of the momentum of the center of mass which is in the direction of the polarization of the light. For ions we show that the integral over the perturbing potential yields $-Nqv$, where N is the degree of ionization, q is the elementary charge, and v is the velocity of the center of mass in the direction which the light wave travels. If the wavelength of the light is large when compared with the size of the vessel which contains ionized atoms or molecules, the equation describing the motion of the center of mass is that of a damped harmonic oscillator. We show that in an external homogeneous electric field, the wave function of the center of mass of an ionized atom or molecule is an Airy function. In an external homogeneous magnetic field, we show that the motion of the center of mass of a neutral molecule is that of a harmonic oscillator with a frequency of $\omega = (N_e q^2 H^2/4Mmc^2)^{1/2}$, where N_e is the number of electrons in the atom or molecule, H is the magnetic field strength, M is the total mass, m is the electronic mass, and c is the velocity of light. If an oscillatory field polarized perpendicular to the steady field is introduced, we show that the transitions are restricted by the usual harmonic-oscillator selection rules, and that the emission rate for spontaneous emission is about 10^{-3} sec^{-1} for the lighter atoms.

I. INTRODUCTION

The motion of the center of mass of atoms and molecules has been ignored as being inconsequential to quantum chemistry. Since chemical reactivity depends on that motion, it should be studied under the variety of conditions to which chemical systems are subjected. Recently we have published several papers[1-3] which described the protonic structure of hydrides where we found it necessary to transform the Hamiltonian to center-of-mass (c.m.) coordinates. As a result of that transformation, we