Scattering of Slow Neutrons by a Liquid*

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The differential cross section for coherent scattering of thermal neutrons by a liquid is given in general by the Fourier transform of a time-displaced radial density function. It is suggested here that, to an adequate degree of approximation, this time-displaced function can be expressed as a convolution of the ordinary radial density function with a self-diffusion function describing the wandering of an atom from an arbitrary initial position. The neutron scattering cross section then becomes the product of the Fourier transforms of these two functions. One of the transforms is the differential cross section for x-ray scattering and describes interference effects, the other governs the energy changes upon scattering. In this development the scatterer can be treated either quantum mechanically or classically. Recoil effects are not provided by the classical treatment, but this is a significant deficiency only in liquids of low atomic weight. Several models for calculating the self-diffusion function are considered, and from these it is suggested that a Gaussian function with a time-dependent width is a reasonable approximation for the case of a simple liquid. The principal features of the width are deduced. Quantization of the scatterer effects the width at small times. At large times the width depends only on the coefficient of self-diffusion of the liquid, and inelastic scattering is suggested as a means of determining this coefficient, as well as other features of atomic movement. The accuracy of the static approximation for determining liquid structures by neutron diffraction is assessed by considering the typical case of liquid lead near its melting point, and is found to be moderately good. The extension of the entire formalism to the case of polyatomic liquids is outlined.

1. INTRODUCTION

THE scattering of slow neutrons by a system of atoms is sufficiently well understood on an abstract level. In the case of solids and dilute gases it is possible to go further and make accurate detailed calculations. In liquids, on the other hand, the atomic dynamics are so complex that specific calculations of the scattering have only been possible with the aid of rather drastic approximations. The simplification that has been commonly used is the so-called static approximation,[1] in which the change of energy of the neutron on scattering is assumed to be negligible compared with the initial energy of the neutron. In this approximation the differential scattering cross section is found to depend only on the ordinary radial density function of the liquid, in complete analogy with the case of x-ray diffraction. No prediction of the spread in energy produced by the scattering can be

made by this method, however, and thus no attack is provided on the problem of determining atomic motions in a liquid through observation of neutron inelastic scattering.

Van Hove[2] has shown that the neutron scattering by an arbitrary system of atoms can be related to a time-displaced distribution function for pairs of atoms. The ordinary radial density is a special case of this function for zero time displacement. The usefulness of this relation has been limited because of the great difficulty of calculating the time-displaced distribution function from first principles. In the present paper a basic approximation is suggested by which the time-displaced function can be calculated from the ordinary radial density function and a self-diffusion function which describes the wandering of an atom away from an arbitrary initial position. The approximation relates the time-displaced function to the convolution of the self-diffusion function with the radial density

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[1] G. Placzek, Phys. Rev. **86**, 377 (1952); G. C. Wick, Phys. Rev. **94**, 1228 (1954).

[2] L. Van Hove, Phys. Rev. **95**, 249 (1954). See also R. J. Glauber, Phys. Rev. **98**, 1692 (1955).

function, and will be referred to as the convolution approximation. With its aid the cross section for neutron scattering into an arbitrary direction and energy will be found to be a product of two functions, one expressing the effect of interference and giving the differential cross section with neglect of energy change (as determined, for example, by x-rays), the other describing the spread in energy and arising directly from the self-diffusion function.

The development to this stage can be carried out by treating the scatterer on a quantum-mechanical basis, or by treating it on a classical basis. The resulting formulas look the same, but in one case their terms have quantum definitions, in the other case they have classical definitions. The meaning of the convolution approximation is more readily apprehended from the classical development, and therefore this approach will be taken up first. The results should be reasonably accurate for scatterers of intermediate or high atomic weight. The quantum development, given in a subsequent section, introduces the effect of recoil during the scattering, and this plays an appreciable role for scatterers of low mass. The approximations employed will not be valid for liquids exhibiting quantum degeneracy, and thus nothing will be said about He II.[3]

As with the time-displaced correlation function, the self-diffusion function cannot be calculated rigorously for a liquid. Instead, this function will be evaluated for a number of simple models, general features of its behavior at small and large times will be demonstrated, and plausible approximations valid for all times will be inferred. These approximations lead to simple expressions for the cross section for scattering with energy and momentum change.

The chief aim in this work is to discover simple formulas which approximate the cross sections reasonably well and depend on a small number of parameters having physical meaning. Such formulas will expedite the use of inelastic neutron scattering as a tool for investigating details of atomic dynamics in liquids.[4] They will also help to give a much needed estimate of the accuracy of radial density functions determined by neutron diffraction through use of the static approximation,[5] and may be of practical value in reactor engineering. The final justification of the approximations employed must be left to experiment.

[3] The highly degenerate quantum liquid is a special case which has recently yielded to treatment. See M. Cohen and R. P. Feynman, Phys. Rev. **107**, 13 (1957), and Palevsky, Otnes, Larsson, Pauli, and Stedman, Phys. Rev. **108**, 1346 (1957).
[4] See also B. N. Brockhouse, Nuovo cimento (to be published).
[5] Such determinations have been reported in the following papers: O. Chamberlain, Phys. Rev. **77**, 305 (1950); P. C. Sharrah and G. P. Smith, J. Chem. Phys. **21**, 228 (1953); Milligan, Levy, and Peterson, Phys. Rev. **83**, 226 (1951); Henshaw, Hurst, and Pope, Phys. Rev. **92**, 1229 (1953); D. G. Henshaw, Phys. Rev. **105**, 976 (1957); Breen, Delaney, Persiani, and Weber, Phys. Rev. **105**, 517 (1957); G. H. Vineyard, J. Chem. Phys. **22**, 1665 (1954).

2. BASIC FORMALISM IN THE CLASSICAL CASE

Consider first a homogeneous classical fluid containing an indefinitely large number of atoms, chemically all alike. The following distribution functions will be of interest: $g(\mathbf{r})$, $G(\mathbf{r},t)$, $G_s(\mathbf{r},t)$, and $G_d(\mathbf{r},t)$. $g(\mathbf{r})$, the ordinary radial density function, is defined as the probability that, if an atom is at the origin, a distinct atom will be found simultaneously within unit volume at $\mathbf{r}$. $G(\mathbf{r},t)$, the time-displaced pair distribution introduced by Van Hove, is defined as the probability that, if an atom is at the origin at time 0, an atom will also be found within unit volume at $\mathbf{r}$ at time t. Note that the atom at $\mathbf{r}$ must be distinct from the one at the origin in the definition of $g(\mathbf{r})$, but need not be in the case of $G(\mathbf{r},t)$. It is further convenient to subdivide $G(\mathbf{r},t)$ into a "self" and a distinct" part $G_s(\mathbf{r},t)$ and $G_d(\mathbf{r},t)$, respectively, where the former gives the probability of finding at $\mathbf{r}$ and time t the atom that was at the origin at time 0, the latter gives the probability of finding at $\mathbf{r}$ and t an atom distinct from the one that was at the origin at time 0. Thus, one has

$$G(\mathbf{r},t) = G_s(\mathbf{r},t) + G_d(\mathbf{r},t). \qquad (1)$$

$G_s(\mathbf{r},t)$ will be called the self-diffusion distribution function. It describes the wandering of an atom away from an arbitrary initial position. Also, from the definitions, one has

$$G_d(\mathbf{r},0) = g(\mathbf{r}), \qquad (2)$$

and

$$G_s(\mathbf{r},0) = \delta(\mathbf{r}). \qquad (3)$$

As t or r approach infinity,[6] the pair correlations vanish in a liquid, and $g(\mathbf{r})$ and $G(\mathbf{r},t)$ approach the mean number density of atoms in the fluid, g_0. Also $G_s(\mathbf{r},t)$ approaches zero.

Now suppose an atom, say atom number 1, is at the origin at time 0, and simultaneously atom number 2 is at $\mathbf{r}'$. There exists a certain probability $H_0(\mathbf{r},\mathbf{r}',t)$ that in an elapsed time t, atom 2 will wander from $\mathbf{r}'$ into a unit volume at $\mathbf{r}$, suffering a net displacement $\mathbf{r} - \mathbf{r}'$. The time-displaced probability $G(\mathbf{r},t)$ can be expressed by the identity

$$G(\mathbf{r},t) = G_s(\mathbf{r},t) + \int g(\mathbf{r}')H_0(\mathbf{r},\mathbf{r}',t)d\mathbf{r}', \qquad (4)$$

where $d\mathbf{r}'$ stands for the volume element $dx'dy'dz'$ and the integration is over all space. The first term on the right of (4) gives the probability that the molecule at the origin at time 0 has migrated to $\mathbf{r}$ in time t, $g(\mathbf{r}')H_0(\mathbf{r},\mathbf{r}',t)d\mathbf{r}'$ is the probability that any other atom is in $d\mathbf{r}'$ at $\mathbf{r}'$ at time 0 and migrates to $\mathbf{r}$ in time t, and the integration sums this over all volume elements $d\mathbf{r}'$.

[6] The symbol r stands for $|\mathbf{r}|$. In most cases to be dealt with, the various distribution functions will have spherical symmetry and will thus depend only on r. The arguments of the functions will be kept as vectors, for the most part, however, because this unifies many of the formulas and increases their generality.

The probability $H_0(\mathbf{r},\mathbf{r}',t)$ is actually conditioned by the known presence of an atom at the origin at time 0, but can be approximated by the probability that an atom starting at $\mathbf{r}'$ will migrate to $\mathbf{r}$ in time t in the absence of knowledge about positions of any other atoms. The latter probability is the self-diffusion distribution function, and hence

$$H_0(\mathbf{r},\mathbf{r}',t) \cong G_s(\mathbf{r}-\mathbf{r}',t). \qquad (5)$$

Inserting (5) into the integral of (4), one has

$$G(r,t) \cong G_s(\mathbf{r},t) + \int g(\mathbf{r}')G_s(\mathbf{r}-\mathbf{r}',t)d\mathbf{r}'. \qquad (6)$$

This is the convolution approximation, the basic approximation of the present paper, and relates the time-displaced distribution function for pairs to the ordinary radial density function and a self-diffusion distribution function.

It is difficult to know the error in this approximation, but qualitative considerations suggest that the chief difference between $H_0(\mathbf{r},\mathbf{r}',t)$ and $G_s(\mathbf{r}-\mathbf{r}',t)$ occurs when t and also r or r' are small. However, when r' is small, $g(\mathbf{r}')$ is small, and the effect of the difference is minimized. When r is small at small times, $G_s(\mathbf{r},t)$ is large, and the second term on the right of Eq. (6) is overshadowed by the first. Errors will also be of both signs in different regions of $\mathbf{r}'$, so there will be some cancellation of errors with integration, $g(\mathbf{r}')$ being always non-negative. Consequently the approximation seems promising, but its ultimate justification will have to depend on experimental test of formulas derived with its help.

The radial distribution function $g(\mathbf{r})$ has been studied extensively, and a number of theoretical schemes for its approximate computation have been developed.[7,8] The distribution $g(\mathbf{r})$ may also be determined by x-ray diffraction.[8,9] No simple analytical expression for it of sufficient generality for our present purposes has been found. The self-diffusion distribution $G_s(\mathbf{r},t)$ has not been studied very much, although Van Hove has given its general features and has calculated it rigorously for the case of a perfect gas. Its determination for an atom in a liquid would be a matter of considerable interest. $G_s(\mathbf{r},t)$ starts as $\delta(\mathbf{r})$ at $t=0$ [Eq. (3)], and, considered as a function of r, spreads and flattens as t increases, having spherical symmetry about the origin. It also obeys the relation[10]

$$G_s(\mathbf{r}, -t) = G_s(\mathbf{r},t). \qquad (7)$$

Several approximate forms of G_s, depending on a small number of parameters, will be discussed subsequently.

[7] H. S. Green, *The Molecular Theory of Fluids* (Interscience Publishers, Inc., New York, 1952), Chap. 3.

[8] G. H. Vineyard, in *Liquid Metals and Solidification* [American Society for Metals, Cleveland (to be published)].

[9] N. S. Gingrich, Revs. Modern Phys. **15**, 90 (1943).

[10] For quantum systems G_s may be complex, and then (7) takes the form $G_s(\mathbf{r}, -t) = G_s^*(\mathbf{r},t)$ if one assumes that the mean momentum of the fluid is zero.

As shown by Van Hove, the differential cross sections per atom, in Born approximation, for the scattering of neutrons from a system of atoms into unit solid angle Ω and unit range of energy ϵ are given by

$$\frac{d^2\sigma_{coh}}{d\Omega d\epsilon} = \frac{a_{coh}^2 k}{\hbar k_0} \int \int [G(\mathbf{r},t) - g_0] \exp[i(\mathbf{\kappa}\cdot\mathbf{r} - \omega t)]d\mathbf{r}dt, \qquad (8)$$

and

$$\frac{d^2\sigma_{inc}}{d\Omega d\epsilon} = \frac{a_{inc}^2 k}{\hbar k_0} \int \int G_s(\mathbf{r},t) \exp[i(\mathbf{\kappa}\cdot\mathbf{r} - \omega t)]d\mathbf{r}dt. \qquad (9)$$

Here the subscript coh refers to coherent scattering, the subscript inc to incoherent scattering (i.e., scattering that is incoherent by virtue of spin or isotope effects); a_{coh} is the bound coherent scattering length, a_{inc} the bound incoherent scattering length, per atom; the incident neutrons have wave number $\mathbf{k}_0$ and energy ϵ_0, the outgoing neutrons have wave number $\mathbf{k}$ and energy ϵ; $\mathbf{\kappa}$ is the scattering vector, $\mathbf{\kappa} = \mathbf{k}_0 - \mathbf{k}$; $\hbar\omega$ is the energy loss of the neutron upon scattering, $\hbar\omega = \epsilon_0 - \epsilon$.

For future use it may be noted that

$$\epsilon_0 = \hbar^2 k_0^2/2m, \qquad (10)$$

$$\epsilon = \hbar^2 k^2/2m, \qquad (11)$$

$$\kappa = k_0[1 + (\epsilon/\epsilon_0) - 2(\epsilon/\epsilon_0)^{\frac{1}{2}} \cos\varphi]^{\frac{1}{2}}, \qquad (12)$$

where m is the mass of the neutron, φ is the angle of scattering (the angle between $\mathbf{k}$ and $\mathbf{k}_0$), and all wave vectors include a factor 2π, so that $k_0 = 2\pi/\lambda_0$, etc.

The cross section (8) has been modified slightly from Van Hove's expression by the subtraction of g_0 in the integrand. This is an artifice to hasten the convergence of the integral, and allows $G(\mathbf{r},t)$ to be defined for an infinitely large sample. The artifice is similar to that commonly employed in the x-ray theory.[8] It changes the cross section by subtraction of a product of δ functions in $\mathbf{\kappa}$ and ω which are nonzero only in a region of angles inaccessible to experiment.

Equations (8) and (9) were first derived for a quantum-mechanical system, and G and G_s are properly defined as averages of certain operators related to the scatterer (see Sec. 5). The classical definitions of G and G_s given above follow directly from the operator definitions when classical behavior is attributed to the scatterer. It is also possible to derive equations of the same form by a semiclassical development in which the scatterer is treated classically from the outset. G and G_s then possess the classical meanings ascribed above as soon as they appear in the formalism. The matter is discussed further at the end of this section.

The convolution approximation for G, Eq. (6), will now be employed to evaluate the coherent cross section as given by Eq. (8). From the fact that

$$\int G_s(\mathbf{r},t)d\mathbf{r} = 1,$$

Eq. (6) can be rewritten

$$G(\mathbf{r},t)-g_0=G_s(\mathbf{r},t)+\int [g(\mathbf{r}')-g_0]G_s(\mathbf{r}-\mathbf{r}',\ t)d\mathbf{r}'. \quad (13)$$

$G-g_0$ is thus a convolution of $g-g_0$ with G_s. Since the desired cross section is a Fourier transform of $G-g_0$, the usual theorem on the Fourier transform of a convolution leads at once to the result

$$\frac{d^2\sigma_{\text{coh}}}{d\Omega d\epsilon}=\frac{a_{\text{coh}}{}^2k}{\hbar k_0}\Gamma_s(\mathbf{\kappa},\omega)[1+\gamma(\mathbf{\kappa})], \quad (14)$$

where

$$\Gamma_s(\mathbf{\kappa},\omega)=\int\int G_s(\mathbf{r},t)\ \exp[i(\mathbf{\kappa}\cdot\mathbf{r}-\omega t)]d\mathbf{r}dt, \quad (15)$$

and

$$\gamma(\mathbf{\kappa})=\int [g(\mathbf{r})-g_0]\exp(i\mathbf{\kappa}\cdot\mathbf{r})d\mathbf{r}. \quad (16)$$

Also the incoherent cross section can now be written

$$\frac{d^2\sigma_{\text{inc}}}{d\Omega d\epsilon}=\frac{a_{\text{inc}}{}^2k}{\hbar k_0}\Gamma_s(\mathbf{\kappa},\omega). \quad (17)$$

Equations (14) and (17) express the cross sections in very simple form in terms of Fourier transforms of the ordinary radial density function and the self-diffusion function. The former contributes a kind of form factor $[1+\gamma(\mathbf{\kappa})]$ which is present in the coherent cross section but not in the incoherent, and expresses the interference effects arising from simultaneous correlations in atomic positions. $\Gamma_s(\mathbf{\kappa},\omega)$, the transform of the self-diffusion distribution, describes the spread of scattered energies caused by motions of the atoms. Equations (14) and (17) are the central equations of this paper.

At this point it is helpful to consider what happens if each atom is rigidly fixed in position, or moves very slowly compared with the velocity of the neutron. $G_s(\mathbf{r},t)$ may then be replaced by $G_s(\mathbf{r},0)=\delta(\mathbf{r})$ [see Eq. (3)] in the integration of Eq. (15), leading to the very simple result

$$\Gamma_s(\mathbf{\kappa},\omega)=\int e^{-i\omega t}dt=2\pi\delta(\omega). \quad (18)$$

The scattering is then purely elastic,

$$\frac{d^2\sigma_{\text{coh}}}{d\Omega d\epsilon}=\frac{a_{\text{coh}}{}^2}{\hbar}\delta(\omega)[1+\gamma(\mathbf{\kappa}_0)], \quad (19)$$

$$\frac{d^2\sigma_{\text{inc}}}{d\Omega d\epsilon}=\frac{a_{\text{inc}}{}^2}{\hbar}\delta(\omega), \quad (20)$$

where $\mathbf{\kappa}_0=\mathbf{k}_0-\mathbf{k}$, with $k=k_0$; from Eq. (12),

$$k_0=2k_0\sin(\varphi/2). \quad (21)$$

The differential cross sections are found by integrating over ϵ, and in the static approximation can be written at once, since $d\epsilon/\hbar=d\omega$,

$$d\sigma_{\text{coh}}/d\Omega=a_{\text{coh}}{}^2[1+\gamma(\mathbf{\kappa}_0)], \quad (22)$$

$$d\sigma_{\text{inc}}/d\Omega=a_{\text{inc}}{}^2. \quad (23)$$

Equation (22) gives a good description of the x-ray diffraction of a monatomic liquid,[8] with a_{coh} replaced by the atomic structure factor, and shows that $1+\gamma(\mathbf{\kappa})$ is simply the (normalized) x-ray scattering from the fluid at scattering vector $\mathbf{\kappa}$. The assumption that the atoms move slowly compared with the velocity of the neutron is the so-called static approximation referred to earlier. When the scatterers are treated classically, this is equivalent to the assumption that the energy change upon scattering is negligible.

A final remark is desirable at this point. As already noted, the cross-section Eqs. (8) and (9) were derived by Van Hove by treating the scatterer as well as the neutron quantum-mechanically. The physical meaning of the classical limit of these equations can be made more evident by giving a different development in which the scatterer is treated by classical mechanics from the beginning. To do this one writes the time-dependent Schrödinger equation for the neutron, with the potential energy depending on the coordinate of the neutron and the coordinates of the atoms of the scatterer. The latter are assumed to be prescribed classical functions of time, describing a classical motion of the scatterer uninfluenced by the neutron. Upon treating this potential-energy term as a time-dependent perturbation, the Schrödinger equation for the neutron can be solved to first order with the aid of the time-dependent Green's function of the equation. Such a process has already been used by Wick[11] to discuss neutron scattering by a lattice. One can now resolve the scattered wave into components corresponding to particular energies and momenta. The square of a component, averaged over an ensemble of motions of the scatterer, gives the differential cross section, and can be manipulated into the form of Eqs. (8) and (9) where $G(\mathbf{r},t)$ and $G_s(\mathbf{r},t)$ have precisely the classical definitions by which they were introduced at the beginning of this section. From this derivation one sees that the scattering has been computed by adding wavelets contributed by each atom of the scatterer at each instant of past time, the frequency of each wavelet being the frequency of the incident wave modified by a Doppler shift occasioned by the velocity of the scatterer at that instant. With a classical $G(\mathbf{r},t)$, the time-displaced correlation formalism predicts a distribution of scattered energies precisely because of the Doppler effect, and it calculates this without allowing any back reaction of the neutron on the scattering system. Such a back reaction would produce recoils of the scattering atoms, thus biasing the Doppler

[11] G. C. Wick, Physik. Z. 38, 402 (1937).

shifts in the direction of lower frequencies. To calculate this recoil effect properly, one has to go to the fully quantum-mechanical formalism, and the semiclassical treatment does not seem capable of leading to useful approximations.

3. SELF-DIFFUSION FUNCTION IN THE CLASSICAL CASE

The self-diffusion function $G_s(\mathbf{r},t)$ and its Fourier transform $\Gamma_s(\boldsymbol{\kappa},\omega)$ will now be considered in more detail. It is possible to calculate G_s rigorously from first principles in only a small number of cases. In the perfect gas an atom maintains its velocity indefinitely, and hence will be displaced by $\mathbf{r}$ in time t if its initial velocity is $\mathbf{r}/t$. The probability of such initial velocity is given by the Maxwellian distribution function, and hence one finds

$$G_s(\mathbf{r},t)=\pi^{-\frac{3}{2}}v_0^{-3}|t|^{-3}\exp[-r^2/(v_0t)^2],$$
$$\text{(perfect gas)} \quad (24)$$

where $v_0=(2k_BT/M)^{\frac{1}{2}}$, with M the mass of an atom, T the temperature of the gas, and k_B Boltzmann's constant. The Fourier inversion of (24) gives

$$\Gamma_s(\boldsymbol{\kappa},\omega)=[2\pi^{\frac{1}{2}}/(\kappa v_0)]\exp[-\omega^2/(\kappa v_0)^2],$$
$$\text{(perfect gas).} \quad (25)$$

In a somewhat similar manner, the isotropic, three-dimensional classical simple harmonic oscillator of frequency ω_1, considered to be in equilibrium at temperature T, is found to possess the self-diffusion function

$$G_s(r,t)=\left[\frac{\omega_1^2}{2\pi v_0^2(1-\cos\omega_1t)}\right]^{\frac{3}{2}}\exp\left[\frac{-\omega_1^2r^2}{2v_0^2(1-\cos\omega_1t)}\right],$$
$$\text{(oscillator)} \quad (26)$$

and this has the Fourier transform

$$\Gamma_s(\boldsymbol{\kappa},\omega)=\pi\exp\left[-\tfrac{1}{2}\left(\frac{\kappa v_0}{\omega_1}\right)^2\right]$$
$$\times\sum_{n=0}^{\infty}\left\{(2-\delta_{0n})I_n\left[\tfrac{1}{2}\left(\frac{\kappa v_0}{\omega_1}\right)^2\right]\right.$$
$$\times[\delta(\omega-n\omega_1)+\delta(\omega+n\omega_1)]\right\}$$
$$\text{(oscillator).} \quad (27)$$

In this equation, $I_n(z)$ is the Bessel function of complex argument and δ_{0n} is the Kronecker delta.

The case of an atom that is in a crystal lattice and whose motion is thus a superposition of a great many simple harmonic vibrations corresponding to the normal modes of the lattice, is a little more complicated but can also be worked out, and gives an essentially simple

result. In the case of a lattice with cubic symmetry, one finds

$$G_s(\mathbf{r},t)=[\pi w^2(t)]^{-\frac{3}{2}}\exp[-r^2/w^2(t)] \quad \text{(lattice).} \quad (28)$$

The time-dependent width of the distribution, squared, is

$$w^2(t)=\frac{4k_BT}{M}\sum_{j=1}^{N}\left(\frac{e_j^x}{\omega_j}\right)^2(1-\cos\omega_jt) \quad \text{(lattice),} \quad (29)$$

where ω_j is the angular frequency of the jth normal mode of the lattice and e_j^x is the x-component of the amplitude of displacement of the atom by the jth mode; normalization is such that $\sum_{j=1}^{N}(e_j^x)^2=1$, the total number of modes being N. On the basis of the simple Debye model with a single Debye frequency ω_D $(\omega_D=k_B\Theta_D/\hbar)$, (29) can be readily evaluated:

$$w^2(t)=[12k_BT/(M\omega_D^2)][1-\sin\omega_Dt/(\omega_Dt)]$$
$$\text{(Debye lattice).} \quad (30)$$

Finally, consider an atom that suffers random alterations of velocity in brief collisions occurring at random times. This atom undergoes a random walk. It has a displacement probability obeying the classical equation of diffusion, in which a single parameter D, the coefficient of self-diffusion, enters:

$$D\nabla^2G_s(\mathbf{r},t)=\partial G_s(\mathbf{r},t)/\partial t. \quad (31)$$

The solution of (31) that corresponds to a point source at the origin at $t=0$ is

$$G_s(\mathbf{r},t)=(4\pi Dt)^{-\frac{3}{2}}\exp[-r^2/(4Dt)]$$
$$\text{(diffusing atom).} \quad (32)$$

This applies for $t\geq0$. The solution for negative times is found from the condition that $G_s(\mathbf{r},t)$ is symmetric in t [Eq. (7)]. The Fourier transform of (32) is

$$\Gamma_s(\boldsymbol{\kappa},\omega)=\frac{2D\kappa^2}{(D\kappa^2)^2+\omega^2} \quad \text{(diffusing atom).} \quad (33)$$

It is a remarkable fact that all of the foregoing distributions, in spite of the variety of models involved, are simple Gaussian functions of r, with widths that depend only on the time. Defining a width $w(t)$ as the radius at which G_s has dropped by e^{-1}, the following values occur:

perfect gas, $w(t)=v_0|t|$;   (34)

oscillator, $w(t)=(v_0/\omega_1)(2-2\cos\omega t)^{\frac{1}{2}}$;   (35)

Debye lattice, $w(t)=[12kT/(M\omega_D^2)]^{\frac{1}{2}}$
$\times[1-\sin\omega_Dt/(\omega_Dt)]^{\frac{1}{2}}$;   (36)

diffusing atom, $w(t)=2(D|t|)^{\frac{1}{2}}$.   (37)

For all cases except the last, $w(t)$, at small t, reduces to $v_0|t|$. This occurs because during very small time intervals the classical particle always behaves as if it were free. The diffusing atom model does not represent
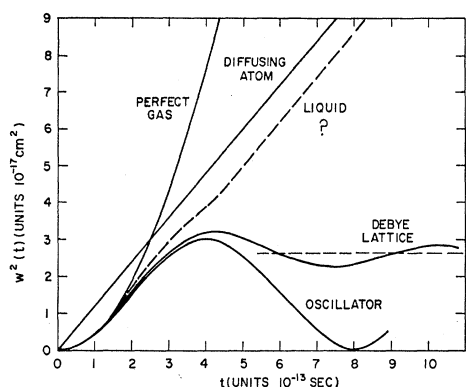
FIG. 1. Square of the width of the self-diffusion function, plotted vs time for several models. Parameters have been chosen to give the best representation for liquid lead at its melting point. Debye period $= 6 \times 10^{-13}$ sec; oscillator period $= 8 \times 10^{-13}$ sec.

any physical situation at short times because it assumes that collisions occur with infinite frequency. In the perfect gas and in the diffusing atom model, the width of the distribution increases without limit as $|t|$ increases; in the oscillator and lattice models, on the other hand, the width remains bounded as $|t|$ increases, and this represents the fact that every atom has a well localized neighborhood in which it always moves. An important consequence is that the scattering from such a model always contains an elastic component, that is, integration of $d^2\sigma/d\Omega d\epsilon$ with respect to ϵ over a region of width $\Delta\epsilon$ about $\epsilon = 0$ gives a contribution that remains finite as $\Delta\epsilon \rightarrow 0$. For the oscillator this can be seen in Eq. (27) as the term in $\delta(\omega)$. A similar term in $\delta(\omega)$ will arise in the Fourier transform of G_s for the lattice. For the perfect gas and the diffusing atom, on the other hand, Γ_s contains no delta function.

To aid in visualizing the various width functions (34)–(37), their squares have been plotted against time in Fig. 1. Parameters have been chosen in this plot to give an approximate representation of liquid lead near its melting point. Corresponding to a Debye temperature of 88°K for solid lead, the Debye temperature for liquid lead has been chosen, somewhat arbitrarily, to be 80°K, and the frequency of the simple harmonic oscillator has been taken to correspond to a characteristic temperature of 60°K. The coefficient of self-diffusion for liquid lead at its melting point is about 3×10^{-5} cm^2/sec.[12] The horizontal dotted line shows the asymptotic value approached by the Debye lattice model at large t.

An atom in a classical liquid is not free nor is it bound like a harmonic oscillator, although it may be bound in this way to a certain degree of approximation for limited periods. Whatever its binding, its displacements must be distributed like that of a free particle, Eq. (24), during very short time intervals. This approximation can only be valid for times that are

[12] L. D. Hall and S. Rothman, Trans. Am. Inst. Mining Met. Engrs. 206, 199 (1956).

small compared to a period τ_D related to a kind of Debye frequency ω_D for the liquid: $\tau_D = 2\pi/\omega_D$. The quantity τ_D would be expected to be of the order of 10^{-13} sec. At the opposite extreme of large $|t|$, an atom will have suffered many collisions and its displacement probability must be well approximated by that of the diffusing atom, Eq. (32).

It will now be proposed that a plausible form of $G_s(\mathbf{r},t)$, valid at all times for the classical liquid, is a Gaussian function of r with a width that varies with time and passes between these two extremes. Thus one should attempt to understand experimental data with the trial function

$$G_s(\mathbf{r},t) = \pi^{-\frac{3}{2}}[w(t)]^{-3} \exp[-r^2/w^2(t)]. \quad (38)$$

The factor $\pi^{-\frac{3}{2}}[w(t)]^{-3}$ is required for normalization. $w(t)$ must be a function of time satisfying the requirements

$$w(t) \rightarrow v_0|t|, \quad |t| \ll \tau_D, \quad (39)$$

$$w(t) \rightarrow 2(D|t|+c)^{\frac{1}{2}}, \quad |t| \gg \tau_D, \quad (40)$$

where c is an undetermined constant. The mean square displacement of the atom after time t is $\frac{3}{2}w^2(t)$, and because of the complicated behavior at intermediate times the asymptotic value of mean square displacement may differ by a constant from the ideal value $6Dt$. The constant c has been introduced to allow for this possibility. Unfortunately no practical theoretical method for determining the precise form of $w(t)$ at intermediate values of t is presently available.[13]

With the Gaussian choice (38) for G_s, the spatial stages of the Fourier transformation can be carried out at once, giving

$$\Gamma_s(\mathbf{\kappa},\omega) = \int_{-\infty}^{\infty} \exp[-i\omega t - \tfrac{1}{4}\kappa^2 w^2(t)]dt. \quad (41)$$

If $\Gamma_s(\mathbf{\kappa},\omega)$ is determined experimentally as a function of ω for one value of κ, then $w(t)$ can be determined from the Fourier inversion of Eq. (41):

$$w^2(t) = \frac{4}{\kappa^2} \ln\left\{\frac{1}{2\pi}\int_{-\infty}^{\infty} \cos(\omega t)\Gamma_s(\mathbf{\kappa},\omega)d\omega\right\}. \quad (42)$$

In using (42) the proper normalization of $\Gamma_s(\mathbf{\kappa},\omega)$ must be observed. This can be insured by using the fact that, from the definitions, $\Gamma_s(0,\omega) = 2\pi\delta(\omega)$. Although the point $\kappa = 0$ is inaccessible to experiment, this condition can be applied at small κ, where the distribution Γ_s will be very sharply peaked about $\omega = 0$. Also the fact that the experimental upper limit of ω is $\epsilon_0/\hbar$ instead of ∞ will not matter in applying (42) unless the distribution is much broader than

[13] C. Christow, Acta Phys. Acad. Sci. Hung. 6 (1956); 7, 51, 67 (1957), has considered the distribution of subsequent positions and velocities of a molecule with known position and velocity. His results to date are limited to the case of the nearly perfect gas, however.

normally expected. In the integration $\cos\omega t$ has been substituted for $\exp(i\omega t)$ because Γ_s on the present theory must be symmetrical in ω at constant κ. Since $w(t)$ is overdetermined by (42), an important check on the assumptions made to this point would be afforded by applying (42) for several different values of κ to see if the same function $w(t)$ is obtained each time.

It would be very interesting to know the true dependence of w on t for an atom in an ordinary liquid. Intuition suggests that a function about like the dashed curve in Fig. 1 should be correct for a typical liquid, since the lattice and oscillator models restrict the atom too severely and the behavior of the extremities of the curve has already been ascertained [Eqs. (39) and (40)]. Mott and Gurney[14] have suggested from consideration of the magnitude of self-diffusion coefficients in liquids that successive vibrations of an atom in a liquid are very little correlated with one another, and the dashed curve of Fig. 1 is in agreement with this assumption. The curve, as drawn, requires c of Eq. (40) to be -10^{-17} cm²/sec. If the atom were to vibrate in a well correlated way for several Debye periods, making occasional diffusion jumps of greater length, c would have to have a much larger negative value.

It has been noted that the coefficient of self-diffusion for liquid lead is about 3×10^{-5} cm²/sec, and it is of interest to inquire about this coefficient for other liquids. Unfortunately the coefficients of self-diffusion have been measured for only a rather small number of liquids, but it is noteworthy that those reported cluster quite closely together, showing far less diversity than self-diffusion coefficients in solids. For monatomic metallic liquids near the melting point, D is almost invariably within the range 10^{-5} to 5×10^{-5} cm²/sec. Thus one would expect the spread of scattered neutrons to be rather similar for a variety of liquids. An increase in temperature of a few hundred degrees centigrade should produce a marked increase in broadening of
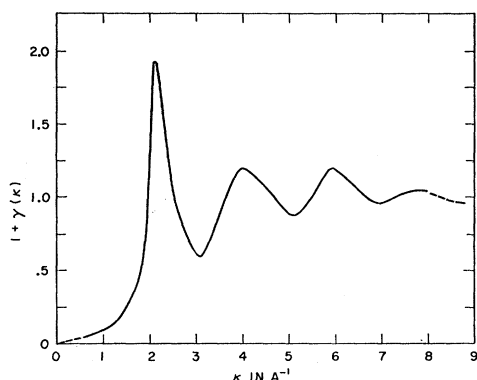
TABLE I. Positions of principle diffraction peaks in lead and approximate energy spread for scattering of neutrons at these positions.

Peak number	κ_0, cm^{-1}	$\Delta\epsilon$ (ev)
1	2.16×10^8	0.0020
2	4.00×10^8	0.0064
3	5.92×10^8	0.0146
4	7.80×10^8	0.0240

the energy distribution. The increase of breadth with temperature should be governed by the activation energy for self-diffusion, which is typically in the range 1000 to 4000 calories/mole for simple metallic liquids.

4. STATIC APPROXIMATION AND STRUCTURE DETERMINATION

It is now possible to assess the accuracy of the static approximation for determining liquid structures by neutron diffraction. To do this it is only necessary to have a theory that gives the inelastic effects in first approximation. From the foregoing discussion the diffusing atom approximation to the self-diffusion function seems reasonable, and has also the great advantage of analytic simplicity. We thus consider the coherent cross section obtained by employing Eq. (33) with Eq. (14):

$$\frac{d^2\sigma_{\mathrm{coh}}}{d\Omega d\epsilon}=\left[\frac{a_{\mathrm{coh}}^2 k}{\hbar k_0}\right]\left[\frac{2D\kappa^2}{(D\kappa^2)^2+\omega^2}\right][1+\gamma(\kappa)]. \quad (43)$$

The factor $1+\gamma(\kappa)$ can be taken from x-ray measurements. A typical curve, for liquid lead at 375°C (observed by Hendus[15]), is shown in Fig. 2. Unfortunately, the experimental accuracy of this curve is not known, but determinations by other investigators are in general agreement with it. For observations at a constant angle of scattering φ, neither k nor κ is strictly constant. However, the principal cause of energy spread is the term in ω, and Eq. (43) thus predicts that the neutrons diffracted at angle φ will be distributed in energy about a most probable energy very near ϵ_0 and with a width in energy at half-maximum, $\Delta\epsilon$, given by

$$\Delta\epsilon\cong2\hbar D\kappa_0^2, \quad (44)$$

where κ_0 is κ for $\epsilon=\epsilon_0$, namely

$$\kappa_0=2k_0\sin(\varphi/2). \quad (45)$$

The values of κ_0 for the first four peaks of $1+\gamma(\kappa_0)$ for liquid lead are given in Table I. Also listed are the energy spreads $\Delta\epsilon$ at these positions, calculated from Eq. (44). Compared with an incident energy of 0.0820 ev, common in diffraction experiments, this spread is seen to be very small at the position of the first peak, but increases rapidly with scattering angle and is quite broad at the position of the fourth peak. It should

FIG. 2. $1+\gamma(\kappa)$ vs κ for liquid lead near its melting point, after x-ray measurements of Hendus.[15]

[14] N. F. Mott and R. W. Gurney, *Reports on Progress in Physics* (The Physical Society, London, 1938), Vol. 5, p. 46.

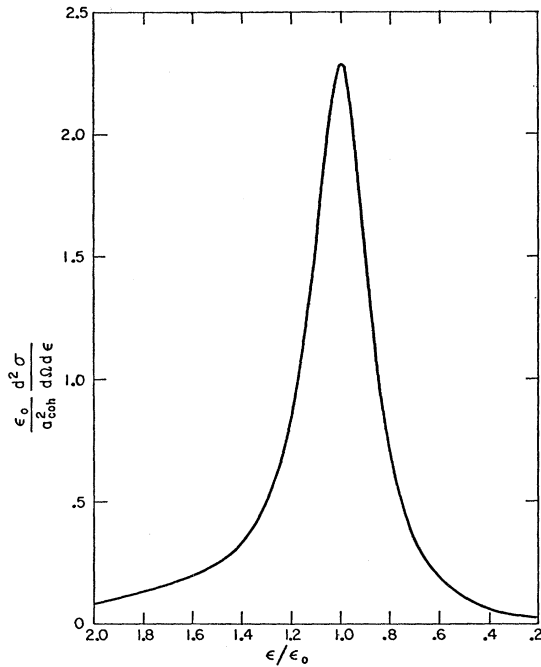[15] H. Hendus, Z. Naturforsch. 2a, 505 (1947).

FIG. 3. Energy distribution of neutrons scattered from liquid lead at angle of fourth peak in Fig. 2, as calculated from Fig. 2 and simple diffusion theory.

be borne in mind that this width is independent of the incident energy ϵ_0 in the approximation being considered.

Because of the factor k/k_0 in Eq. (43), and because κ also depends on ϵ at constant φ, the energy distribution at a particular angle of scattering is not quite symmetrical and the width is not quite as given by Eq. (44). These complications are more important at high angles than at low. The actual energy distribution of neutrons scattered by liquid lead at an angle corresponding to the fourth peak ($\kappa_0 = 7.8 \times 10^8$ cm^{-1}), assuming $\epsilon_0 = 0.082$ ev, and employing Eq. (43) and the data of Fig. 2, is shown in Fig. 3. The differential cross section, made dimensionless by the factor ϵ_0/a_{coh}^2, is plotted against ϵ/ϵ_0. The asymmetry is appreciable only in the wings of the distribution, and the width at half-maximum is about 4% less than the value given in Table I.

To compute the differential cross section $d\sigma_{coh}/d\Omega$, Eq. (43) must be integrated with respect to ϵ at constant φ. Here a difficulty is encountered: the integral diverges as ϵ approaches ∞. This comes about because of the incorrect behavior at small t of the width function $w(t)$ that has been used. There should be no discontinuity in slope of $w(t)$ at $t=0$, and correct behavior here leads to a Γ_s which vanishes exponentially at large ϵ. Consequently the integrations must be broken off at a finite ϵ if Eq. (43) is to be used. Analytic work is not feasible at this stage anyway, and we shall be content to point out qualitative and semiquantitative results. In the present formalism, integrating $d^2\sigma_{coh}/$

$d\Omega d\epsilon$ over ϵ is crudely equivalent to viewing the function $1+\gamma(\kappa)$ through a resolution function, $(k/k_0)\Gamma_s(\kappa,\omega)$, whose width is strongly dependent on κ. Where the resolution function is narrow (small κ), it is nearly equivalent to a delta function, and this converts $1+\gamma(\kappa)$ into $1+\gamma(\kappa_0)$. Where the width is greater, the resolution function tends principally to level out $1+\gamma(\kappa)$, lowering the peaks, filling in the valleys, and leaving points of inflection almost unchanged. The question of when the resolution function is effectively a delta function is somewhat delicate, because at lower angles the peaks and valleys in $1+\gamma(\kappa)$ are also much sharper. Furthermore the sharpest peaks in $1+\gamma(\kappa)$ may already have been rounded by instrumental effects in the x-ray determinations.

An idea of the magnitude of the effects in question can be had by considering further the example of liquid lead. The peak in Fig. 3 can be integrated numerically, assuming that the cross section is negligible beyond the energy limits of the drawing. The result is that the actual differential cross section for neutrons is, in this direction, about 10% lower than the value given by the static approximation. The error of the static approximation diminishes with decreasing angle, and at the first peak, in spite of the greater sharpness of the peak, the static approximation is found to be too large by only about $\frac{1}{2}\%$. The latter number is dependent on the second derivative of the x-ray differential cross section at the first peak, a number which certainly is not very accurately known. Thus the figure $\frac{1}{2}\%$ should be considered as only an illustrative estimate.

5. BASIC FORMALISM IN THE QUANTUM CASE

The foregoing development has been based entirely on the classical approximation to the Van Hove time-displaced pair distribution, $G(\mathbf{r},t)$. It is only in this approximation that G can be interpreted as the probability of finding an atom at $\mathbf{r}$ and t after an atom has been observed at the origin at time zero. Consequently it is only in this context that the basic convolution approximation, given by Eq. (6), has been shown to make sense. The classical development has been presented first because it is more easily visualized and most of the desired results can be got from it. The theory can actually be generalized, however, and the convolution approximation can be developed on a purely quantum basis, in which the functions G and G_s are given their proper, nonclassical, definitions. The chief physical interest of such a development is this: In the classical approximation, the behaviors of G and G_s are incorrect at small t and, moreover, no recoil effects in the scattering are accounted for. This is so because the classical approximation results only when $\hbar/M$ is made to approach zero, where M is the mass of a scattering atom. Thus, going to the classical approximation means assuming that the scatterer is very massive, and this is precisely the case in which recoil is absent. For atoms of intermediate or high

atomic number, M is sufficiently large that the recoil effects are very small and their neglect is unimportant in most respects. For very light atoms and neutron energies of interest in diffraction experiments, recoil appears to play an observable role. Thus, for liquid helium at $4°K$ Hurst and Henshaw[16] have found that 0.076-ev neutrons are scattered with about the same average energy loss as if they had been scattered from He gas at the same temperature, and this amounts to 0.002 ev at a scattering angle of $20°$ and 0.017 ev at an angle of $60°$. The latter energy loss is sufficient to reduce the differential cross section quite appreciably, essentially because of the state-density factor k/k_0 [see Eq. (14)]. It would be highly desirable to extend the development given in the first part of this paper so as to include such effects in a unified way.

In the fully quantum mechanical treatment, the functions G and G_s are Fourier transforms of the expectation values of certain operators. Thus, if the scatterer consists of N atoms and $r_l(t)$ denotes the Heisenberg operator representing the position of the lth atom at time t, one defines the operators

$$\Omega_{lj}(\mathbf{\kappa},t) = \exp[-i\mathbf{\kappa}\cdot\mathbf{r}_l(0)]\exp[i\mathbf{\kappa}\cdot\mathbf{r}_j(t)]. \quad (46)$$

Then, as shown by Van Hove,[2] the functions G and G_s, to be used in Eqs. (8) and (9) for determining cross sections are found from the Ω operator as follows:

$$G(\mathbf{r},t) = \frac{1}{(2\pi)^3 N}\int d\mathbf{\kappa}\,\exp(-i\mathbf{\kappa}\cdot\mathbf{r})\sum_{l,j=1}^{N}\langle\Omega_{lj}(\mathbf{\kappa},t)\rangle; \quad (47)$$

$$G_s(\mathbf{r},t) = \frac{1}{(2\pi)^3 N}\int d\mathbf{\kappa}\,\exp(-i\mathbf{\kappa}\cdot\mathbf{r})\sum_{l=1}^{N}\langle\Omega_{ll}(\mathbf{\kappa},t)\rangle. \quad (48)$$

The angular brackets in these expressions denote quantum mechanical expectation values. The quantum mechanical definition of $g(\mathbf{r})$ is obtained from the relation

$$g(\mathbf{r}) = G(\mathbf{r},0) - \delta(\mathbf{r}). \quad (49)$$

Because of the commutativity of $\mathbf{r}_l(0)$ and $\mathbf{r}_j(0)$, $g(\mathbf{r})$ is purely real and retains exactly the physical significance already ascribed to it.

To obtain a quantum mechanical derivation of the convolution approximation, one splits the summation in Eq. (47) into two parts, one part in which $l=j$, and a second part in which $l\neq j$. The first part gives $G_s(\mathbf{r},t)$, by Eq. (48). The operator $\Omega_{lj}(\mathbf{\kappa},t)$ in the second part is rewritten with the help of the relation

$$\Omega_{lj}(\mathbf{\kappa},t) = \Omega_{lj}(\mathbf{\kappa},0)\Omega_{jj}(\mathbf{\kappa},t), \quad (50)$$

which follows from the insertion of the identity operator

$$\exp[i\mathbf{\kappa}\cdot\mathbf{r}_j(0)]\exp[-i\mathbf{\kappa}\cdot\mathbf{r}_j(0)]$$

between the two factors on the right of Eq. (46).

[16] D. G. Hurst and D. G. Henshaw, Phys. Rev. **100**, 994 (1955).

At this stage one has, rigorously,

$$G(\mathbf{r},t) = G_s(\mathbf{r},t) + \frac{1}{(2\pi)^3 N}\int d\mathbf{\kappa}$$

$$\times\exp(-i\mathbf{\kappa}\cdot\mathbf{r})\sum_{l\neq j=1}^{N}\langle\Omega_{lj}(\mathbf{\kappa},0)\Omega_{jj}(\mathbf{\kappa},t)\rangle. \quad (51)$$

The basic approximation that corresponds to Eq. (6) of the classical development is to assume that

$$\langle\Omega_{lj}(\mathbf{\kappa},0)\Omega_{jj}(\mathbf{\kappa},t)\rangle\cong\langle\Omega_{lj}(\mathbf{\kappa},0)\rangle\langle\Omega_{jj}(\mathbf{\kappa},t)\rangle, \quad (52)$$

i.e., the expectation value of a certain product can be set equal to the product of expectation values. This is the way in which the quantum mechanical definition of G can incorporate the assumption that the occurrence of a second atom at $\mathbf{r}'$ from a given atom and the migration of the second atom to $\mathbf{r}$ in time t are statistically independent events. Next, inserting (47) in the right-hand side of Eq. (49), one finds

$$g(\mathbf{r}) = \frac{1}{(2\pi)^3 N}\int d\mathbf{\kappa}\,\exp(-i\mathbf{\kappa}\cdot\mathbf{r})\sum_{l\neq j=1}^{N}\langle\Omega_{lj}(\mathbf{\kappa},0)\rangle. \quad (53)$$

Using the basic approximation (52) in Eq. (51) and remembering that all N atoms are alike, (53) and (48) can now be employed to produce the result

$$G(\mathbf{r},t)\cong G_s(\mathbf{r},t) + \int g(\mathbf{r}')G_s(\mathbf{r}-\mathbf{r}',\ t)d\mathbf{r}', \quad (54)$$

which is of precisely the same form as Eq. (6), but here G, G_s, and g have all been defined quantum mechanically, by Eqs. (47), (48), and (49). Thus the convolution approximation for G in terms of G_s and g has been derived without appeal to any classical concepts. The classical version, Eq. (6), can be derived afresh by considering the limit of Eq. (54) when the de Broglie wavelengths associated with the scatterer become sufficiently small that G, G_s, and g acquire their classical meanings.

The $g(\mathbf{r})$ defined for a quantum mechanical system by Eq. (49) or Eq. (53) is the same function that is found from x-ray diffraction, and hence is the same as that considered earlier. G_s, on the other hand, is complex for a quantum mechanical system, and the relative importance of its imaginary part is greatest at small values of t.

It is illuminating to consider the exact form of G_s for some simple quantum mechanical systems. Van Hove[2] has shown that for a perfect gas and also for an atom in a crystal lattice the quantum mechanical G_s functions are again Gaussian in $\mathbf{r}$. For the perfect gas, the width is

$$w(t) = v_0[t^2 - i\hbar t/(k_B T)]^{\frac{1}{2}}, \quad (55)$$

and for the isotropic, three-dimensional simple harmonic oscillator of frequency ω_1, a special case of the atom in a

lattice, the width works out to be

$$w(t) = \left(\frac{2\hbar}{M\omega_1}\right)^{\frac{1}{2}} \left[\frac{\exp(\hbar\omega_1/k_BT)+1}{\exp(\hbar\omega_1/k_BT)-1}(1-\cos\omega_1 t)\right.$$
$$\left. -i\sin\omega_1 t\right]^{\frac{1}{2}}. \quad (56)$$

The imaginary components distinguish these widths from the values computed classically, Eqs. (34) and (35). For times large compared with $\hbar/(k_BT)$ the perfect gas width (55) becomes identical with the classical value (34), while for times large compared with $\hbar/(k_BT)$ and for temperatures high compared with the characteristic temperature $\hbar\omega_1/k_B$ the oscillator width (56) assumes its classical value (35). The additional requirement on the temperature, in the case of the oscillator, arises because it is necessary for many quantum states of the system to be excited in order for it to assume classical behavior. At small enough times the imaginary term dominates these expressions, because the imaginary part of $w^2(t)$ becomes proportional to t while the real part becomes proportional to t^2. Indeed this can be shown to be a general property of any system described by a time-independent Hamiltonian and possessing no mass transport. One expands the operator $\Omega_{ll}(\kappa,t)$ in powers of t after writing

$$\exp[i\boldsymbol{\kappa}\cdot\mathbf{r}_l(t)] = \exp[itH/\hbar]\exp[i\boldsymbol{\kappa}\cdot\mathbf{r}_l(0)]$$
$$\times\exp[-itH/\hbar], \quad (57)$$

where H is the Hamiltonian of the system. A generalized width of the distribution, $w_g(t)$, is defined by the relation

$$w_g^2(t) = \frac{2}{3}\int r^2 G_s(\mathbf{r},t)d\mathbf{r}. \quad (58)$$

One can then show, under the assumption that the system is isotropic on the average, that

$$w_g^2(t) = -i\frac{2\hbar}{M}t + \frac{2}{3M^2}\langle p^2\rangle t^2 + \cdots, \quad (59)$$

where $\mathbf{p}$ is the operator representing the momentum of any one atom. The term linear in t, which dominates at small t, is thus of purely quantum mechanical origin, while the term quadratic in t survives in the classical limit.

Since the atom undergoing a random walk (diffusing atom) has been suggested as a model for calculating the self-diffusion function to first approximation in the classical case, we will next inquire into the possibility of carrying this model into the quantum realm. In the classical model a particle moves under the influence of a viscous force and a driving force, the driving force being of a stochastic nature, fluctuating so that its average values in time intervals Δt are independent of one another and such that its long time average is

zero. The stochastic driving force represents the "random" impacts of other atoms, while the viscous force represents the correlated retarding impacts of other atoms which develop when the atom has a finite velocity. One postulates that the position of the atom $\mathbf{r}(t)$ obeys the Langevin equation[17]

$$d^2\mathbf{r}/dt^2 + \eta d\mathbf{r}/dt = \mathbf{f}(t), \quad (60)$$

where η is a coefficient of viscous damping, and $M\mathbf{f}(t)$ is the stochastic driving force. As a model for our purpose, we shall now suppose that $\mathbf{r}(t)$ and its time derivatives are to be interpreted as Heisenberg operators in the standard way, and $\mathbf{r}(t)$ will be used for $\mathbf{r}_l(t)$ in Eqs. (46) and (48). $\mathbf{f}(t)$ will be supposed to be a c number subject to the same stochastic behavior as in the classical theory of the Brownian motion.[17] The operator Eq. (60), being linear, is integrated in the same way as the corresponding classical equation:

$$\mathbf{r}(t) - \mathbf{r}(0) = \frac{\mathbf{p}(0)}{M\eta}(e^{-\eta t} - 1)$$
$$-\frac{1}{\eta}\int_0^t dt' \mathbf{f}(t')[e^{-\eta(t-t')} - 1], \quad (61)$$

where $\mathbf{p}(0)$ is the momentum operator for the atom at $t=0$.

From (61) one evaluates the commutator

$$[\boldsymbol{\kappa}\cdot\mathbf{r}(0),\ \boldsymbol{\kappa}\cdot\mathbf{r}(t)] = i\hbar M^{-1}\eta^{-1}\Phi(-\eta t)\kappa^2, \quad (62)$$

where

$$\Phi(x) = e^x - 1. \quad (63)$$

Since the commutator is a c number, the product of exponentials in $\Omega_{ll}(\kappa,t)$ can be rewritten by the rule

$$e^A e^B = e^{\frac{1}{2}[A,B]}e^{(A+B)}.$$

Setting $A = i\boldsymbol{\kappa}\cdot\mathbf{r}(0)$ and $B = i\boldsymbol{\kappa}\cdot\mathbf{r}(t)$ one finds

$$\langle\Omega_{ll}(\boldsymbol{\kappa},t)\rangle = \exp[\frac{1}{2}i\hbar M^{-1}\eta^{-1}\Phi(-\eta t)\kappa^2]$$
$$\times\langle\exp[-iM^{-1}\eta^{-1}\Phi(-\eta t)\boldsymbol{\kappa}\cdot\mathbf{p}(0)]\rangle$$
$$\times\langle\exp[-iX(t)]\rangle, \quad (64)$$

where

$$X(t) = \eta^{-1}\int_0^t dt' \boldsymbol{\kappa}\cdot\mathbf{f}(t')\Phi(\eta t' - \eta t). \quad (65)$$

The second factor on the right of (64) is evaluated in a straightforward manner. In the third factor the angular brackets designate an average over the fluctuations in $f(t)$. From the stochastic assumptions concerning $\mathbf{f}$ and the central limit theorem, $X(t)$ is known to be normally distributed about the mean value 0. Its standard deviation can be calculated from (65) and is

$$\langle X^2(t)\rangle = \frac{1}{3}\kappa^2\eta^{-2}\langle f^2\rangle\Delta t[\frac{1}{2}\eta^{-1}\Phi(-2\eta t)$$
$$-2\eta^{-1}\Phi(-\eta t)+t], \quad (66)$$

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[17] S. Chandrasekhar, Revs. Modern Phys. **15**, 1 (1943).

where $\langle f^2 \rangle$ is the mean square value of $\mathbf{f}$ and Δt is a small interval of the order of the autocorrelation time of $\mathbf{f}(t)$. With this information the third factor in (64) can now be evaluated. When the result is inserted in Eq. (48), the self-diffusion function $G_s(\mathbf{r},t)$ is again found to be a Gaussian in $\mathbf{r}$ with the width

$$w(t) = \left\{ \frac{2i\hbar}{M\eta}\Phi(-\eta t) + \frac{2k_BT}{M\eta^2}\Phi^2(-\eta t) \right.$$
$$\left. + D\left[-\frac{2}{\eta}\Phi(-2\eta t) + \frac{8}{\eta}\Phi(-\eta t) + 4t \right] \right\}^{\frac{1}{2}}. \quad (67)$$

Here $\frac{1}{3}\eta^{-2}\langle f^2 \rangle \Delta t$ has been replaced by D, the diffusion coefficient in this model. For small times $\Phi(-\eta t) \cong -\eta t$, and the first term on the right of (67) gives an imaginary contribution to $w^2(t)$, of purely quantum mechanical origin. The second term is essentially classical, and commences as t^2. These terms are in agreement with the first two terms of the generalized series (59). The final term in (67) is proportional to t^3 at small t. At large t, $\Phi(-\eta t) \to 1$ and

$$w(t) \to \left\{ -\frac{2i\hbar}{M\eta} + \frac{2k_BT}{M\eta^2} - \frac{6D}{\eta} + 4Dt \right\}^{\frac{1}{2}}, \quad (68)$$

which is the same as the form (40) describing the simple classical diffusing atom except that the constant c is complex. Equations (67) and (68) have been derived on the implicit assumption that $t \geq 0$. For negative t one may determine w from the relation

$$w(-t) = w^*(t). \quad (69)$$

Assuming the validity of the Einstein relationship

$$\eta = kT/MD, \quad (70)$$

which insures that the velocity distribution of the atom becomes Maxwellian after a long time, the asymptotic width (68) may be simplified to

$$w(t) \to [-2i\hbar M^{-1}\tau + 4D(t-\tau)]^{\frac{1}{2}}, \quad (71)$$

$$\tau = 1/\eta. \quad (72)$$

It would be desirable to have the Fourier transform of the self-diffusion function with width given by Eq. (67), but the time integration therein is intractable. As a useful approximation, bringing out the major features of the model, (67) can be replaced by two separate forms valid in the realm of small and large t, respectively. For t small compared with the characteristic time τ the linear quantum term predominates in $w^2(t)$, and for t large compared with τ the linear classical term and the constants predominate. Thus, as a very rough description of the quantum mechanical diffusion model, we choose

$$w^2(t) = -2i\hbar M^{-1}t, \quad 0 \leq t \leq \tau, \quad (73)$$

$$w^2(t) = -2i\hbar M^{-1}\tau + 4D(t-\tau), \quad t > \tau. \quad (74)$$

Transforming the Gaussian defined by (69), (73), and (74), one finds

$$\Gamma_s(\kappa,\omega) = \frac{2\sin(\omega\tau - \hbar\kappa^2\tau/2M)}{\omega - \hbar\kappa^2/2M}$$
$$+ \frac{2\kappa^2 D\cos(\omega\tau - \hbar\kappa^2\tau/2M) - 2\omega\sin(\omega\tau - \hbar\kappa^2\tau/2M)}{(\kappa^2 D)^2 + \omega^2}. \quad (75)$$

The first term on the right of Eq. (75) comes from the small time region $|t| < \tau$, the second term from the large time region $|t| > \tau$. Considering this expression as a function of ω at fixed κ, one discerns two distinct types of behavior, depending on whether κ is small or large. Define a critical parameter

$$\kappa_c = (k_B T/MD^2)^{\frac{1}{2}}. \quad (76)$$

The two types of behavior occur in the regions $\kappa \ll \kappa_c$ and $\kappa \gg \kappa_c$, respectively. In the former $\tau \ll 1/(\kappa^2 D)$, in the latter $\tau \gg 1/(\kappa^2 D)$. In the region of small κ, the first term of (75), considered as a function of ω, is low and broad, the second is high and narrow. The numerator of the second term is approximately $2\kappa^2 D$ for ω in the range of the peak, hence the peak is almost symmetrical about $\omega = 0$, and has a width $\kappa^2 D$ and a Lorentzian shape, just as in the classical diffusion model [see the middle factor in Eq. (43)]. Here there is essentially no recoil effect. In the region of large κ, on the other hand, the roles of the two terms in (75) are reversed, the first being high and narrow, the second low and broad. The high peak is symmetrical about ω_0, where

$$\omega_0 = \hbar\kappa^2/(2M). \quad (77)$$

It is seen that here there is an average loss of energy on scattering, which is caused by recoil of the scatterer, and the magnitude of the loss, ω_0, is precisely the same as for a free atom or a Maxwellian gas. This agrees with the observations of Hurst and Henshaw on liquid helium.[16] The detailed shapes of the peaks are certainly not reliable in the present approximation. In particular Eq. (75) predicts fine structure in the cross section which can be traced to the discontinuities in slope of the $w(t)$ employed, and which is undoubtedly spurious. Also the width of the peak in the case of large κ is independent of κ. If one improves the approximation (73) by including higher powers of t the width of this peak becomes an increasing function of κ, although the extent of its dependence on κ can be determined only by more detailed calculations.

The transition from bound-particle to free-particle behavior at about κ_c is entirely reasonable, and represents the fact that, for large momentum changes of the neutron, the recoil is sufficient to outweigh the binding of the atoms in the liquid. For liquid lead near its melting point, $\kappa_c = 5.4 \times 10^8$ cm^{-1}, which occurs in about the middle of the scattering pattern for neutrons

of wavelength 1 angstrom. From (77) it is seen that the amount of energy shift varies inversely with the mass of the scattering atom. For lead, this shift at κ_c is only about 3% of the peak breadth at this point, and hence is negligible. For atoms ten times lighter than lead, the recoil shift is beginning to be appreciable and should not be neglected for atomic masses much below 20, except in cases of abnormally small momentum change.

6. GENERALIZATION TO POLYATOMIC SYSTEMS

The time-displaced formalism and the convolution approximation are easily generalized to apply to the case of a liquid made up of several atomic species. For completeness the basic formulas will be presented here. Previously used symbols will be given a suffix n (or m) to refer to the nth (or mth) atomic species. Summations over these indices will always run from 1 to J, where J is the number of species present. $G(\mathbf{r},t)$ must be generalized to a set of functions $G^{nm}(\mathbf{r},t)$, the classical limit of which is the probability of finding an n-type atom at $\mathbf{r}$ and t if an m-type atom was at the origin at time zero. The quantum mechanical definition in terms of operators Ω_{ij} follows from an obvious generalization of Eq. (47). The self-diffusion function for the nth species will be written $G_s{}^n(\mathbf{r},t)$, and we let $g^{nm}(\mathbf{r}) = G^{nm}(\mathbf{r},0)$. The convolution approximation is expressed by the relations

$$G^{nm}(\mathbf{r},t) \cong \delta_{nm} G_s{}^n(\mathbf{r},t) + \int g^{nm}(\mathbf{r}') G_s{}^n(\mathbf{r}-\mathbf{r}',\ t) d\mathbf{r}',$$

$$n, m = 1 \cdots J. \quad (78)$$

The coherent and incoherent scattering cross sections are

$$\frac{d^2\sigma_{coh}}{d\Omega d\epsilon} = \frac{k}{hk_0} \sum_{n,m} x_m a_{coh}{}^n a_{coh}{}^m \int [G^{nm}(\mathbf{r},t) - g_0{}^n]$$

$$\times \exp[i(\mathbf{\kappa}\cdot\mathbf{r} - \omega t)] d\mathbf{r} dt, \quad (79)$$

$$\frac{d^2\sigma_{inc}}{d\Omega d\epsilon} = \frac{k}{hk_0} \sum_n x_n (a_{inc}{}^n)^2 \int G_s{}^n(\mathbf{r},t)$$

$$\times \exp[i(\mathbf{\kappa}\cdot\mathbf{r} - \omega t)] d\mathbf{r} dt, \quad (80)$$

where x_m is the fraction of the atoms that are of type m.

Defining the Fourier transform of $G_s{}^n(\mathbf{r},t)$ as $\Gamma_s{}^n(\mathbf{\kappa},\omega)$ and the transform of $g^{nm}(\mathbf{r}) - g_0{}^n$ as $\gamma^{nm}(\mathbf{\kappa})$, in analogy with Eqs. (15) and (16), the convolution approximation leads to the simplified expressions for the cross sections

$$\frac{d^2\sigma_{coh}}{d\Omega d\epsilon} \cong \frac{k}{hk_0} \sum_{n,m} x_m a_{coh}{}^n a_{coh}{}^m \Gamma_s{}^n(\mathbf{\kappa},\omega)[\delta_{nm} + \gamma^{nm}(\mathbf{\kappa})], \quad (81)$$

$$\frac{d^2\sigma_{inc}}{d\Omega d\epsilon} = \frac{k}{hk_0} \sum_n x_n (a_{inc}{}^n)^2 \Gamma_s{}^n(\mathbf{\kappa},\omega). \quad (82)$$

In the classical diffusing atom model, species n has the self-diffusion coefficient D_n, and the function $\Gamma_s{}^n$ is given by

$$\Gamma_s{}^n(\mathbf{\kappa},\omega) = \frac{2D_n\kappa^2}{(D_n\kappa^2)^2 + \omega^2}. \quad (83)$$

The general physical content of these relations seems to require no further discussion at this stage.

7. SUMMARY AND CONCLUSIONS

Expressions for the coherent scattering cross sections of simple liquids for slow neutrons have been derived on the basis of two types of approximations: (a) the convolution approximation, which expresses the time-displaced pair distribution in terms of the radial density function and a self-diffusion function for a single atom; (b) a Gaussian approximation for the self-diffusion function. The width of the Gaussian is time-dependent and has certain general properties at large and at small times, and a behavior at intermediate times which can be inferred from simple models. The most sophisticated model considered in detail here has been the quantum analog of Brownian motion. A slightly cruder model is afforded by the classical Brownian motion. The neutron scattering is seen to involve a spread in outgoing energies with a width that increases rapidly with increasing scattering angle, and with a reduction in average energy attributable to recoil. The recoil is greater for light substances and large momentum changes, and is unimportant for atoms of intermediate or high atomic mass. The formulas derived here do not show the recoil effect unless the scatterer is treated quantum mechanically. The spread in energy produced by scattering at any given angle appears to be determined primarily by the coefficient of self-diffusion for the liquid, and may well afford a useful independent method of measuring this coefficient.

The development presented here has the merit of giving simple results which contain a good deal of physical meaning and appear to possess the right qualitative features. Because of the several approximations employed, the accuracy of the final formulas cannot be stated with certainty, and it is highly desirable that they be subjected to experimental tests.