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Theory of Slow Neutron Scattering by Liquids. I*

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Based on Van Hove's formalism, a general discussion of scattering in liquids has been given. The scattering cross section has been expressed in terms of velocity correlation functions; in particular, for the incoherent scattering cross section it is shown that in the Gaussian approximation for Van Hove's $G_s(\mathbf{r},t)$ function, only a knowledge of the velocity autocorrelation function $\langle\mathbf{v}(0)\cdot\mathbf{v}(t)\rangle_T$ is necessary. The departure from the Gaussian approximation is expressed in terms of higher order velocity correlation functions. A derivation of an approximate formula for the width function of the Gaussian $G_s(\mathbf{r},t)$, suggested earlier by the authors, has been given. The frequency spectrum of the velocity autocorrelation function has been introduced, and it has been shown that, as a consequence of the fluctuation-dissipation relations, the spectral representation of the width function is formally identical with that obtained earlier for a harmonic solid. The first few moments of the energy transfer have been discussed. Some of these moments have been shown to satisfy certain relations which involve only experimentally observable quantities; and hence, these relations can be used as a check on the internal consistency of the experimental data.

I. INTRODUCTION

THE theory of neutron scattering by an interacting system in terms of the space-time correlation function $G(\mathbf{r},t)$ has been given by Van Hove.[1] Besides being elegant, Van Hove's formalism has the merit that it is very useful for interpreting the scattering data for systems such as liquids for which an exact calculation of the scattering is too complicated. This possibility arises from the fact that the function $G(\mathbf{r},t)$ in the classical case has a very simple physical meaning and it has known limiting forms for both small and large times. These considerations have led and guided many authors[2–7] in recent years to propose certain dynamic models of the liquid state to interpret the scattering data.

Instead of discussing the scattering in terms of Van Hove's G function, it is often more convenient to discuss it in terms of what we call the intermediate scattering function $F(\boldsymbol{\kappa},t)$ which is the space transform of the function $G(\mathbf{r},t)$, $\hbar\boldsymbol{\kappa}$ being the momentum transfer. The corresponding transform of the self-part of $G(\mathbf{r},t)$ is denoted by $F_s(\boldsymbol{\kappa},t)$. It is shown in Sec. V that $F_s(\boldsymbol{\kappa},t)$ can be written as an exponential, the exponent being an infinite series in κ^2. The coefficient of κ^2 in this series is simply related to the two-velocity correlation function $\langle\mathbf{v}(0)\cdot\mathbf{v}(t)\rangle_T$ and the coefficient of κ^4 to the four-velocity correlation function and so on. The behavior of $F_s(\boldsymbol{\kappa},t)$ for the two limiting cases: (i) $t\rightarrow 0$ and (ii) $t\rightarrow\infty$ is discussed. The condition under which the Gaussian approximation for the G_s function is valid, has been derived. The κ^4 term in the series is the first term in the non-Gaussian correction. So far, it has not been possible to calculate the magnitude of this correction; however, it should be possible to estimate this correction experimentally.

In the Gaussian approximation a rigorous quantum-mechanical expression for the width function is derived (Sec. VI). This width function is complex. By making use of the fluctuation-dissipation theorem, discussed in detail in Sec. III, the scattering cross section $S_{\rm inc}(\boldsymbol{\kappa},\omega)$ can be expressed as a Fourier transform of a real function $H_s(\boldsymbol{\kappa},t)$. A very good approximation is obtained for the width function of $H_s(\boldsymbol{\kappa},t)$, expressed in terms of the classical two-velocity correlation function. In the Gaussian approximation, the problem of calculating the incoherent scattering cross section for almost all liquids is thus reduced to a classical calculation of the velocity autocorrelation function $\langle\mathbf{v}(0)\cdot\mathbf{v}(t)\rangle_T$.

It is shown in Sec. VII how in a natural way one can introduce in the formalism the frequency spectrum $f(\omega)$ of the velocity autocorrelation function. In fact, by making use of the fluctuation-dissipation theorem one notices that the width function of $H_s(\boldsymbol{\kappa},t)$ for a liquid has exactly the same form as that for a harmonic solid. Thus it is legitimate to characterize the dynamics of a liquid by this frequency distribution function analogous to the case of a solid.

The first four moments of $S_{\rm inc}(\boldsymbol{\kappa},\omega)$, first given by Placzek,[8] have been rederived in Sec. IV in a simple manner and further, relations between the second and the third moments and between the second and the fourth moments are given which do not contain the potential and involve only experimentally measurable quantities. In the coherent case, a similar relation between the second and the third moments is established.

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These relations may be of utility in checking the internal consistency of the experimental data.

Section II contains a general discussion of the basic mathematical formulae, and also a discussion of Vineyard's "convolution approximation"[4] for coherent scattering. A recent article by Nelkin[9] contains a review of certain aspects of the material discussed in Sec. II, III, and IV.

II. MATHEMATICAL FORMULATION

According to Van Hove[1] the scattering cross section can be written in the following form:

$$d^2\sigma_{\mathrm{coh}}/d\Omega d\omega = N a_{\mathrm{coh}}^2 (k/k_0) S_{\mathrm{coh}}(\boldsymbol{\kappa},\omega), \tag{1}$$

$$d^2\sigma_{\mathrm{inc}}/d\Omega d\omega = N a_{\mathrm{inc}}^2 (k/k_0) S_{\mathrm{inc}}(\boldsymbol{\kappa},\omega), \tag{2}$$

where

$$S_{\mathrm{coh}}(\boldsymbol{\kappa},\omega) = \frac{1}{2\pi}\int \exp[i(\boldsymbol{\kappa}\cdot\mathbf{r}-\omega t)]G(\mathbf{r},t)d\mathbf{r}dt, \tag{3}$$

$$S_{\mathrm{inc}}(\boldsymbol{\kappa},\omega) = \frac{1}{2\pi}\int \exp[i(\boldsymbol{\kappa}\cdot\mathbf{r}-\omega t)]G_s(\mathbf{r},t)d\mathbf{r}dt. \tag{4}$$

The cross section has in the conventional way been separated into a coherent and an incoherent part and the two scattering lengths are denoted by a_{coh} and a_{inc}. $\hbar\omega$ and $\hbar\boldsymbol{\kappa}$ are the energy and momentum transfers, and they are connected to the incident and final wave vectors of the neutron, $\mathbf{k}_0$ and $\mathbf{k}$, respectively, through the relations

$$\begin{aligned} \boldsymbol{\kappa} &= \mathbf{k}_0 - \mathbf{k}, \\ \omega &= (\hbar/2m)(k_0^2 - k^2), \end{aligned} \tag{5}$$

where m is the neutron mass and N denotes the total number of atoms in the scattering system. For simplicity, we restrict ourselves to monatomic systems.

The introduction of the G functions by Van Hove was mainly due to the fact that these functions could be interpreted directly in simple physical terms.[1,10] It is, however, for many purposes more convenient to analyze the space transform of $G(\mathbf{r},t)$,

$$F(\boldsymbol{\kappa},t) = \int \exp(i\boldsymbol{\kappa}\cdot\mathbf{r})G(\mathbf{r},t)d\mathbf{r}, \tag{6}$$

and the corresponding transform of $G_s(\mathbf{r},t)$, henceforth denoted by $F_s(\boldsymbol{\kappa},t)$. The scattering functions $S_{\mathrm{coh}}(\boldsymbol{\kappa},\omega)$ and $S_{\mathrm{inc}}(\boldsymbol{\kappa},\omega)$ are then simply the time transforms of $F(\boldsymbol{\kappa},t)$ and $F_s(\boldsymbol{\kappa},t)$, respectively. In fact, in the derivation of the scattering cross section one normally arrives at $F(\boldsymbol{\kappa},t)$ first.

The general definitions are:

$$F(\boldsymbol{\kappa},t) = \frac{1}{N}\sum_{l,j} \langle \exp[-i\boldsymbol{\kappa}\cdot\mathbf{r}_l(0)] \exp[i\boldsymbol{\kappa}\cdot\mathbf{r}_j(t)]\rangle_T, \tag{7}$$

$$F_s(\boldsymbol{\kappa},t) = \frac{1}{N}\sum_{l} \langle \exp[-i\boldsymbol{\kappa}\cdot\mathbf{r}_l(0)] \exp[i\boldsymbol{\kappa}\cdot\mathbf{r}_l(t)]\rangle_T. \tag{8}$$

Here $\mathbf{r}_l(t)$ is the position vector of the lth atom in the Heisenberg representation. $\langle\cdots\rangle_T$ means that both quantum mechanical and statistical averages should be taken. In (7) summation over all atoms j is performed and finally an averaging over all atoms l, and in (8) only this averaging has to be made. For a system in statistical equilibrium the final averaging is immaterial if surface effects are neglected. The properties of the functions $F(\boldsymbol{\kappa},t)$ and $G(\mathbf{r},t)$ for $t=0$ are well known and need no comment. However, it is worthwhile to recall that for $|t|\to\infty$ both $F(\boldsymbol{\kappa},t)$ and $F_s(\boldsymbol{\kappa},t)$ tend to zero except in the case of a solid, and in that case, they tend to a finite limit with the remarkable consequence that both $S_{\mathrm{coh}}(\boldsymbol{\kappa},\omega)$ and $S_{\mathrm{inc}}(\boldsymbol{\kappa},\omega)$ have a $\delta(\omega)$ singularity. It is experimentally well established that a finite fraction of the neutrons are scattered without any energy change. In a liquid, where diffusion cannot be neglected, we do not have any elastic scattering in the same sense as for a solid. This, however, does not exclude the possibility of having a pronounced peak in the energy spectrum with a finite width around the incident energy. It is obvious that the width of this "quasi-elastic" peak depends sensitively on how $F(\boldsymbol{\kappa},t)$ $[F_s(\boldsymbol{\kappa},t)]$ tends to zero for $|t|\to\infty$. On the other hand, scattering corresponding to large energy transfers will mainly depend on the properties of $F(\boldsymbol{\kappa},t)$ $[F_s(\boldsymbol{\kappa},t)]$ for small times.

To analyze the F functions in more detail, it is convenient to express them in terms of velocity correlation functions. For that purpose, we rewrite $F(\boldsymbol{\kappa},t)$ in the following way[11]:

$$\begin{aligned} F(\boldsymbol{\kappa},t) &= \textstyle\sum_j \langle \exp\{-i\boldsymbol{\kappa}\cdot[\mathbf{r}_0(0)-\mathbf{r}_j(0)]\} \exp[-i\boldsymbol{\kappa}\cdot\mathbf{r}_j(0)] \\ &\quad \times \exp(iHt/\hbar) \exp[i\boldsymbol{\kappa}\cdot\mathbf{r}_j(0)] \exp(-iHt/\hbar)\rangle_T \\ &= \exp(i\hbar\kappa^2 t/2M) \textstyle\sum_j \langle \exp\{-i\boldsymbol{\kappa}\cdot[\mathbf{r}_0(0)-\mathbf{r}_j(0)]\} \\ &\quad \times \exp(iH'_j t/\hbar) \exp(-iHt/\hbar)\rangle_T, \end{aligned} \tag{9}$$

where $H'_j = H + \hbar(\boldsymbol{\kappa}\cdot\mathbf{v}_j)$, H being the Hamiltonian of the system and $\mathbf{v}_j$ the velocity operator of the jth atom. We have here made use of the relation

$$\exp(-i\boldsymbol{\kappa}\cdot\mathbf{r}) f(\mathbf{p},\mathbf{r}) \exp(i\boldsymbol{\kappa}\cdot\mathbf{r}) = f(\mathbf{p}+\hbar\boldsymbol{\kappa},\mathbf{r}), \tag{10}$$

$f(\mathbf{p},\mathbf{r})$ being any function of the momentum and position operators.

Taking the term $j=0$ in (9), we obtain the corresponding expression for $F_s(\boldsymbol{\kappa},t)$. This alternative definition of $F(\boldsymbol{\kappa},t)$ and of $F_s(\boldsymbol{\kappa},t)$ has often been used before.

Before we conclude this section, in which up to now we have been concerned with the formal aspect only, we shall mention briefly the approximations which have been used for $F(\boldsymbol{\kappa},t)$ and for $F_s(\boldsymbol{\kappa},t)$.

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[9] M. S. Nelkin, Proceedings of the Symposium on Slow Neutron Scattering, International Atomic Energy Agency, Vienna, 1960 (unpublished).

[10] L. Van Hove, Physica 24, 404 (1958).

[11] We are here dropping the averaging $(1/N)\sum_l$ in Eq. (7) and putting index $l=0$.

Making the assumption that the bracket in Eq. (9) can be broken up into a product of two factors

$$\langle\exp[-i\boldsymbol{\kappa}\cdot(\mathbf{r}_0-\mathbf{r}_j)]\rangle_T\langle\exp(iH'_jt/\hbar)\,\exp(-iHt/\hbar)\rangle_T,$$

we obtain the following relation between $F(\boldsymbol{\kappa},t)$ and $F_s(\boldsymbol{\kappa},t)$:

$$F(\boldsymbol{\kappa},t)=F(\boldsymbol{\kappa},0)F_s(\boldsymbol{\kappa},t). \tag{11}$$

This is the "convolution approximation" first used by Vineyard[4] to take care of interference effects in an approximate way. From Vineyard's derivation, it is clear that this approximation holds for very small values of κ. For large κ, on the other hand, the interference effects are negligible and this is indeed in accordance with Eq. (11), for $F(\boldsymbol{\kappa},0)\rightarrow 1$ when $\kappa\rightarrow\infty$. In most experiments using cold neutrons, the conditions have, however, been such that κ is neither very small nor very large.

Equation (11) has been used earlier in calculating the scattering from lead.[7] As has been mentioned there, even for intermediate values of κ the observed variation with κ of the scattered intensity for small energy transfer can be accounted for reasonably well on the basis of this approximation.

It is a fact that Vineyard's approximation violates the following classical relation between the second moments of $S_{\text{coh}}(\boldsymbol{\kappa},\omega)$ and $S_{\text{inc}}(\boldsymbol{\kappa},\omega)$[12,13]:

$$\int_{-\infty}^{\infty}\omega^2S_{\text{coh}}(\boldsymbol{\kappa},\omega)d\omega=\int_{-\infty}^{\infty}\omega^2S_{\text{inc}}(\boldsymbol{\kappa},\omega)d\omega, \tag{12}$$

$\boldsymbol{\kappa}$ being kept constant during the integration. However, this fact should not be used as an argument for a complete rejection of the approximation because, as mentioned above, it may be of some utility in the region of small energy transfer. This region does not contribute significantly to the integrals in Eq. (12). It is certainly true that for larger energy transfer the approximation is not valid; it overestimates the interference effects[14]; the reason being that instead of Eq. (11) we have for $t=0$, in the classical limit

$$d^2F(\boldsymbol{\kappa},t)/dt^2=dF_s(\boldsymbol{\kappa},t)^2/dt^2. \tag{13}$$

This leads directly to Eq. (12). Egelstaff[15] has suggested a modification of Vineyard's approximation for small times in such a way that Eq. (13) is satisfied and furthermore the corresponding relation between the fourth time derivatives of $F(\boldsymbol{\kappa},t)$ and $F_s(\boldsymbol{\kappa},t)$ for $t=0$ is approximately fulfilled.

In most applications made so far, one has also made simplifying assumptions about $F_s(\boldsymbol{\kappa},t)$.[2–7] One can expand the bracket $\langle\cdots\rangle$ in Eq. (9) ($j=0$) in powers of κ^2 as follows (See Sec. IV):

$$\langle e^{iH't/\hbar}e^{-iHt/\hbar}\rangle_T$$
$$=1-\kappa^2\int_0^t dt_1\int_0^{t_1}dt_2\,\langle v_\kappa(t_2)v_\kappa(t_1)\rangle_T+\cdots. \tag{14}$$

All the coefficients of the odd powers of κ involve an average of an odd power of the velocity and thus disappear. In (14) $v_\kappa(t)$ stands for the velocity component along the direction of $\boldsymbol{\kappa}$. In Sec. V, it will be shown how one can treat in a consistent way the infinite series in (14) and obtain as a first approximation

$$\langle e^{iH't/\hbar}e^{-iHt/\hbar}\rangle_T$$
$$=\exp\left\{-\kappa^2\int_0^t dt_1\int_0^{t_1}dt_2\,\langle v_\kappa(t_2)v_\kappa(t_1)\rangle_T\right\}. \tag{15}$$

Using this approximation in the expression for $F_s(\boldsymbol{\kappa},t)$ we get the so called "Gaussian approximation"

$$F_s(\boldsymbol{\kappa},t)=\exp[-\kappa^2\gamma_1(t)], \tag{16}$$

where

$$\gamma_1(t)=-i(\hbar t/2M)+\tfrac{1}{3}\int_0^t(t-t_1)\langle\mathbf{v}(0)\cdot\mathbf{v}(t_1)\rangle_Tdt_1. \tag{17}$$

In going from (15) to (16) and (17) we have made use of the isotropy of the system and the time translation invariance of $\langle\mathbf{v}(t_2)\cdot t_1(\mathbf{v}_1)\rangle_T$. A further discussion of $\gamma_1(t)$ is given in Sec. VI.

III. THE FLUCTUATION-DISSIPATION THEOREM

It was first pointed out by Schofield[16] that there exists a simple relation between the real and the imaginary parts of Van Hove's G function, and that a violation of that relation leads to a violation of the condition of detailed balance for the scattering cross section. In the treatment of transport properties according to Callen and Welton,[17] Kubo,[18] and others, a relation connecting the fluctuations and the dissipation in a system plays an important role. That relation is a consequence of the Hermiticity of the quantities involved. The relation obtained by Schofield is a dissipation-fluctuation theorem, which was rederived in an earlier paper[19] using the technique of Callen and Welton. Van Hove[10] did connect the imaginary part of his G function with the linear response in the density of the system due to the interaction with the incident neutrons, but he did not show how such an analysis leads to a considerable simplification of the scattering problem.

It can be shown[19] that the imaginary and real parts of $F_s(\boldsymbol{\kappa},t)$ are related as follows:

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[12] See the following section on moments.

[13] P. G. De Gennes, Physica **25**, 825 (1959).

[14] See reference 7, Fig. 4.

[15] P. A. Egelstaff, Proceedings of the Symposium on Slow Neutron Scattering, International Atomic Energy Agency, Vienna, 1960, paper IS, p. 7 (unpublished).

[16] P. Schofield, Phys. Rev. Letters **4**, 239 (1960).

[17] H. B. Callen and T. A. Welton, Phys. Rev. **83**, 34 (1951).

[18] R. Kubo, J. Phys. Soc. Japan **12**, 570 (1957).

[19] K. S. Singwi and A. Sjölander, Phys. Rev. **120**, 1093 (1960).

$$\int_{-\infty}^{\infty} e^{-i\omega t}\,\mathrm{Im}F_s(\boldsymbol{\kappa},t)dt = -i\tanh(\beta\omega)\int_{-\infty}^{\infty} e^{-i\omega t}\,\mathrm{Re}F_s(\boldsymbol{\kappa},t)dt, \tag{18}$$

where $\beta=\hbar/2k_BT$; Eq. (18) implies the following formal relation

$$\mathrm{Im}F_s(\boldsymbol{\kappa},t)=-\tan(\beta d/dt)\,\mathrm{Re}F_s(\boldsymbol{\kappa},t). \tag{19}$$

The same equation holds, of course, also for $G_s(\mathbf{r},t)$, which is obtained from $F_s(\boldsymbol{\kappa},t)$ through a Fourier transformation in $\boldsymbol{\kappa}$. It is obvious from Eq. (19) that any assumptions regarding $\mathrm{Re}F_s(\boldsymbol{\kappa},t)$ imply automatically through (19) a certain assumption about $\mathrm{Im}F_s(\boldsymbol{\kappa},t)$. From the definition, it follows that $\mathrm{Re}F_s(\boldsymbol{\kappa},t)$ is an even function of t.[20]

When applying Eq. (19), a considerable simplification can be made by introducing a new function $H_s(\boldsymbol{\kappa},t)$, defined by

$$H_s(\boldsymbol{\kappa},t)=F_s(\boldsymbol{\kappa},\,t+i\beta). \tag{20}$$

Expanding F_s in powers of β and making use of Eq. (19) leads to the following relation:

$$H_s(\boldsymbol{\kappa},t)=\exp(i\beta d/dt)F_s(\boldsymbol{\kappa},t) =\sec(\beta d/dt)\,\mathrm{Re}F_s(\boldsymbol{\kappa},t). \tag{21}$$

A less formal expression is obtained by taking the Fourier transform in t of Eq. (21), and one obtains an equation of the same type as (18).

Due to the fact that $\sec(\beta d/dt)$ is a real operator, the function $H_s(\boldsymbol{\kappa},t)$ will be real. This is a consequence of Eq. (19). On the other hand, the reverse is also true; assuming $H_s(\boldsymbol{\kappa},t)$ real leads to Eq. (19). The latter formulation is more useful when calculating the scattering cross section. By simply modifying the path of integration while taking the time Fourier transform of $F_s(\boldsymbol{\kappa},t)$ the scattering cross section $S_{\mathrm{inc}}(\boldsymbol{\kappa},\omega)$ can be written in the form

$$S_{\mathrm{inc}}(\boldsymbol{\kappa},\omega)=e^{\beta\omega}\frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-i\omega t}H_s(\boldsymbol{\kappa},t)dt, \tag{22}$$

originally given by Schofield.[16]

$H_s(\boldsymbol{\kappa},t)$ is a real and an even function of t and thus the integral above is even in ω. The exponential factor $e^{\beta\omega}$ is essential to satisfy the condition of detailed balance. It is now possible either to try to find approximate expressions for $H_s(\boldsymbol{\kappa},t)$ directly or, which seems more suitable, first to find $\mathrm{Re}F_s(\boldsymbol{\kappa},t)$ approximately and then determine $H_s(\boldsymbol{\kappa},t)$ through Eq. (21).

The same arguments as used for $F_s(\boldsymbol{\kappa},t)$ can be applied to $F(\boldsymbol{\kappa},t)$ and the relation between the real and imaginary parts holds unchanged.

The fluctuation-dissipation theorem is most often given for Hermitian operators. If $A(t)$ and $B(t)$ are two Hermitian Heisenberg operators and Boltzmann's statistics is applicable, Eq. (19) holds for the statistical average $\langle A(0)B(t)\rangle_T$.[21] This more general formulation will be used when we discuss the Gaussian approximation for $F_s(\boldsymbol{\kappa},t)$.[22]

IV. THE MOMENTS OF $S(\kappa,\omega)$

The first four moments of $S_{\mathrm{inc}}(\boldsymbol{\kappa},\omega)$ were first given by Placzek[8] using an expansion of $F_s(\boldsymbol{\kappa},t)$ in powers of t. We shall here give a simpler derivation of these moments.

Incoherent Case

The moments of $S_{\mathrm{inc}}(\boldsymbol{\kappa},\omega)$ can be derived very simply by using the expression for $F_s(\boldsymbol{\kappa},t)$, obtained from Eq. (9) by retaining the self-term $j=0$. Introducing the notation

$$A(\boldsymbol{\kappa},t)=\exp(iH't/\hbar)\exp(-iHt/\hbar), \tag{23}$$

it is easy to derive the following equation for $A(\boldsymbol{\kappa},t)$:

$$\partial A(\boldsymbol{\kappa},t)/\partial t=i\kappa A(\boldsymbol{\kappa},t)v_\kappa(t), \tag{24}$$

$v_\kappa(t)$ being the projection of $\mathbf{v}(t)$ along $\boldsymbol{\kappa}$. Equation (24) can be solved by iteration, giving the formal solution

$$A(\boldsymbol{\kappa},t)=\sum_{n=0}^{\infty}(i\kappa)^n\int_0^t dt_1\int_0^{t_1}dt_2\cdots \int_0^{t_{n-1}}dt_n\,\{v_\kappa(t_n)\cdots v_\kappa(t_1)\}. \tag{25}$$

Denoting $\hbar\kappa^2/2M$ by ω_R, we have from (25) and from the definition of $S_{\mathrm{inc}}(\boldsymbol{\kappa},\omega)$

$$\int_{-\infty}^{\infty}\exp[i(\omega-\omega_R)t]S_{\mathrm{inc}}(\boldsymbol{\kappa},\omega)d\omega =\sum_{n=0}^{\infty}(-\kappa^2)^n\int_0^t dt_1\cdots \times\int_0^{t_{2n-1}}dt_{2n}\langle v_\kappa(t_{2n})\cdots v_\kappa(t_1)\rangle_T. \tag{26}$$

Due to thermal averaging, all odd powers of v_κ have disappeared.

We shall introduce the notation

$$\langle f(\omega)\rangle_{\mathrm{inc}}=\int_{-\infty}^{\infty} f(\omega)S_{\mathrm{inc}}(\boldsymbol{\kappa},\omega)d\omega. \tag{27}$$

Then by repeated differentiation of Eq. (26) with

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[20] In an unpublished paper, R. Becker has recently discussed the fluctuation-dissipation theorem in greater detail and has explicitly given a number of different relations connected to Eqs. (18) and (19).

[21] See W. Bernard and H. B. Callen, Revs. Modern Phys. **31**, 1017 (1959).

[22] The relation between the real and imaginary parts also holds for the case $B^\dagger=A$, even though A may not be Hermitian if the operators depend only on the position coordinates. This fact has actually been used in the derivation of Eq. (18).

respect to t and finally putting $t=0$, we get

$$\begin{aligned}\langle 1\rangle_{\text{inc}}&=1,\\ \langle(\omega-\omega_R)\rangle_{\text{inc}}&=\kappa\langle v_\kappa\rangle_T=0,\\ \langle(\omega-\omega_R)^2\rangle_{\text{inc}}&=\kappa^2\langle v_\kappa{}^2\rangle_T,\\ \langle(\omega-\omega_R)^3\rangle_{\text{inc}}&=-i\kappa^2\langle v_\kappa dv_\kappa/dt\rangle_T,\\ \langle(\omega-\omega_R)^4\rangle_{\text{inc}}&=\kappa^4\langle v_\kappa{}^4\rangle_T-\kappa^2\langle v_\kappa d^2v_\kappa/dt^2\rangle_T.\end{aligned}\tag{28}$$

It is then possible to show that if U is the potential energy of the system and z is the component of the position vector of a particle in the κ-direction,

$$\begin{aligned}\langle(\omega-\omega_R)^3\rangle_{\text{inc}}&=(\omega_R/M)\langle\partial^2U/\partial z^2\rangle_T,\\ \langle(\omega-\omega_R)^4\rangle_{\text{inc}}&=\kappa^4\langle v_\kappa{}^4\rangle_T+(\kappa^2/M^2)\langle(\partial U/\partial z)^2\rangle_T.\end{aligned}\tag{29}$$

These are the same as the expressions given by Placzek where $\langle\omega^n\rangle_{\text{inc}}$ are given instead of $\langle(\omega-\omega_R)^n\rangle_{\text{inc}}$ as above.

Neglecting ω_R, and calculating the statistical averages in (29) classically, leads to De Gennes[13] expressions for the moments of $S_{\text{inc}}(\boldsymbol{\kappa},\omega)$.

The utility of the above moments from the experimental point of view is that they provide a relation between various observable quantities and hence a check on the accuracy of the experimentally obtained $S_{\text{inc}}(\boldsymbol{\kappa},\omega)$. This will be seen from the following.

Using a theorem[23] which gives the quantum mechanical correction to the classical statistical average of any dynamical variable, one has

$$\begin{aligned}\langle v_\kappa{}^2\rangle_T=&(k_BT/M)\\ &\times\{1+(\hbar^2/12Mk_B{}^3T^3)\langle(\partial U/\partial z)^2\rangle_{\text{cl}}+\cdots\},\end{aligned}\tag{30}$$

where $\langle\cdots\rangle_{\text{cl}}$ means the classical thermal average. To this approximation, the velocity distribution has been shown to retain its Maxwellian form (see the foregoing reference) and hence

$$\begin{aligned}\langle v_\kappa{}^4\rangle_T=3\langle v_\kappa{}^2\rangle_T{}^2=&3(k_BT/M)^2\\ &\times\{1+(\hbar^2/6Mk_B{}^3T^3)\langle(\partial U/\partial z^2)\rangle_{\text{cl}}+\cdots\}.\end{aligned}\tag{31}$$

Using

$$\langle(\partial U/\partial z)^2\rangle_{\text{cl}}=k_BT\langle\partial^2U/\partial z^2\rangle_{\text{cl}},\tag{32}$$

and eliminating $\langle\partial^2U/\partial z^2\rangle_T$ in Eqs. (28) and (29), we get

$$\begin{aligned}&\langle(\omega-\omega_R)^2\rangle_{\text{inc}}\\ &\quad=(2\omega_Rk_BT/\hbar)+(\hbar/6k_BT)\langle(\omega-\omega_R)^3\rangle_{\text{inc}}+\cdots,\end{aligned}\tag{33}$$

and

$$\begin{aligned}\langle(\omega-\omega_R)^2\rangle_{\text{inc}}=&(2\omega_Rk_BT/\hbar)\\ &-\omega_R{}^2+(\hbar^2/12k_B{}^2T^2)\langle(\omega-\omega_R)^4\rangle_{\text{inc}}+\cdots.\end{aligned}\tag{34}$$

Coherent Case

The algebra here is more involved than in the above case due to the presence of the term $\exp[-i\boldsymbol{\kappa}\cdot(\mathbf{r}_0-\mathbf{r}_j)]$ in Eq. (9).

Using the notation $\gamma(\boldsymbol{\kappa})$ for $[F(\boldsymbol{\kappa},0)-1]$, a quantity which is obtained from x-ray or neutron-diffraction experiments, we first get

$$\begin{aligned}\langle 1\rangle_{\text{coh}}&=1+\gamma(\boldsymbol{\kappa}),\\ \langle(\omega-\omega_R)\rangle_{\text{coh}}&=-\omega_R\gamma(\boldsymbol{\kappa}),\\ \langle(\omega-\omega_R)^2\rangle_{\text{coh}}&=\kappa^2\textstyle\sum_j\langle v_{\kappa0}\exp[-i\boldsymbol{\kappa}\cdot(\mathbf{r}_0-\mathbf{r}_j)]v_{\kappa j}\rangle_T,\\ \langle(\omega-\omega_R)^3\rangle_{\text{coh}}&=\kappa^3\textstyle\sum_j\langle v_{\kappa0}\exp[-i\boldsymbol{\kappa}\cdot(\mathbf{r}_0-\mathbf{r}_j)]v_{\kappa j}{}^2\rangle_T,\\ &\quad-i\kappa^2\textstyle\sum_j\langle v_{\kappa0}\exp[-i\boldsymbol{\kappa}\cdot(\mathbf{r}_0-\mathbf{r}_j)]\dot{v}_{\kappa j}\rangle_T.\end{aligned}\tag{35}$$

(Note that the second of these equations implies $\langle\omega\rangle_{\text{coh}}=\omega_R=\langle\omega\rangle_{\text{inc}}$.)

Again using the theorem mentioned above, it can be shown that

$$\begin{aligned}\langle(\omega-\omega_R)^2\rangle_{\text{coh}}=&(2\omega_Rk_BT/\hbar)+\omega_R{}^2\gamma(\boldsymbol{\kappa})\\ &+(\hbar\omega_R/6Mk_BT)\textstyle\sum_j\langle\exp[-i\boldsymbol{\kappa}\cdot(\mathbf{r}_0-\mathbf{r}_j)]\\ &\times(\partial^2U/\partial z_0\partial z_j)\rangle_{\text{cl}}+\cdots\end{aligned}\tag{36}$$

$$\begin{aligned}\langle(\omega-\omega_R)^3\rangle_{\text{coh}}=&(\omega_R/M)\textstyle\sum_j\langle\exp[-i\boldsymbol{\kappa}\cdot(\mathbf{r}_0-\mathbf{r}_j)]\\ &\times(\partial^2U/\partial z_0\partial z_j)\rangle_{\text{cl}}+\cdots.\end{aligned}$$

Hence

$$\begin{aligned}\langle(\omega-\omega_R)^2\rangle_{\text{coh}}=&(2\omega_Rk_BT/\hbar)+\omega_R{}^2\gamma(\boldsymbol{\kappa})\\ &+(\hbar/6k_BT)\langle(\omega-\omega_R)^3\rangle_{\text{cl}}.\end{aligned}\tag{37}$$

In Eqs. (33), (34), and (37), we have taken into account the recoil term ω_R and the first-order quantum correction to the value of $\langle v_\kappa{}^2\rangle_T$. The recoil effect can certainly not be neglected whenever the mass of the atom is small. As regards the quantum correction to $\langle v_\kappa{}^2\rangle_T$ it is negligible in most liquids. By using the expression for a solid with an appropriate value for the Debye temperature, we can roughly estimate this quantum correction. We get

$$\langle v_\kappa{}^2\rangle_T-\langle v_\kappa{}^2\rangle_{\text{cl}}\approx(\langle v_\kappa{}^2\rangle_{\text{cl}}/20)(\theta_D/T)^2,\ \langle v_\kappa{}^2\rangle_{\text{cl}}=k_BT/M.\tag{38}$$

In the exceptional case of liquid Neon ($T_M=24$°K, $\theta_D{}^{\text{solid}}=64$°K) and possibly in the case of liquid Argon ($T_M=84$°K, $\theta_D{}^{\text{solid}}=80$°K) we may expect the quantum correction to be significant.

V. TRANSFORMATION OF $F_s(\boldsymbol{\kappa},t)$

To be able to analyze the scattering function $S_{\text{inc}}(\boldsymbol{\kappa},\omega)$ in greater detail, we will bring it in a form which, at least in some cases, is more suitable than that given in Eq. (9). We are primarily interested in the thermal average of $A(\boldsymbol{\kappa},t)$ given in (23). Using the expansion in Eq. (25), we get

$$\begin{aligned}\langle A(t)\rangle_T=&\sum_{n=0}^{\infty}(-\kappa^2)^n\int_0^t dt_1\int_0^{t_1}dt_2\cdots\\ &\times\int_0^{t_{2n-1}}dt_{2n}\langle v_\kappa(t_{2n})\cdots v_\kappa(t_1)\rangle_T.\end{aligned}\tag{39}$$

We will adopt a time-cluster expansion which is very similar to the cluster expansion in distance introduced by Ursell[24] and Mayer[25] when discussing the thermo-

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[23] See for instance L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon Press, New York, 1958) p. 102.

[24] H. D. Ursell, Proc. Cambridge Phil. Soc. 23, 685 (1927).

[25] J. E. Mayer, J. Chem. Phys. 5, 67 (1937).

dynamic properties of dense systems. We express the higher order correlation functions in terms of those of lower order as follows:

$$\begin{aligned}\langle v_\kappa(t_4)\cdots v_\kappa(t_1)\rangle_T &= \{u_2(t_4,t_3)u_2(t_2,t_1)+u_2(t_4,t_2)u_2(t_3,t_1)\\ &\quad +u_2(t_4,t_1)u_2(t_3,t_2)\}+u_4(t_4,t_3,t_2,t_1), \end{aligned}\tag{40}$$

$$\begin{aligned}\langle v_\kappa(t_6)\cdots v_\kappa(t_1)\rangle_T &= \{u_2(t_6,t_5)u_2(t_4,t_3)u_2(t_2,t_1)+\cdots\}\\ &\quad +\{u_4(t_6,t_5,t_4,t_3)u_2(t_2,t_1)+\cdots\}\\ &\quad +u_6(t_6,t_5,t_4,t_3,t_2,t_1). \end{aligned}\tag{41}$$

Here $u_2(t_2,t_1)=\langle v_\kappa(t_2)v_\kappa(t_1)\rangle_T$ and the higher order functions u_4, u_6, etc., are successively defined by the above equations. The dots in the first curly bracket in (41) imply that all possible products of u_2 functions have been taken. Similarly, in the second bracket in (41) all possible products of u_2 and u_4 functions are implied.

The u functions are defined in such a way that they are essentially zero unless all the times involved are close together. For instance, in (40) whenever one of the times is far from the other three, $\langle v_\kappa(t_4)\cdots v_\kappa(t_1)\rangle_T$ is zero; and when the four times cluster together in pairs so that the pairs are far from each other, this bracket breaks up into one of the products appearing inside the curly bracket in (40). Thus $u_4(t_4,t_3,t_2,t_1)$ vanishes except when all four times are clustered together. We notice that in Eq. (39) we have the restriction $t\geqslant t_1\geqslant t_2\geqslant\cdots$ for $t>0$, and $t\leqslant t_1\leqslant t_2\leqslant\cdots$ for $t<0$.

In the general case, we write

$$\langle v_\kappa(t_{2n})\cdots v_\kappa(t_1)\rangle_T =\sum (u_{p_1}\cdots u_{p_1})(u_{p_2}\cdots u_{p_2})\cdots(u_{p_\nu}\cdots u_{p_\nu}). \tag{42}$$

Here $\langle v_\kappa(t_{2n})\cdots v_\kappa(t_1)\rangle_T$ is broken up into products of lower order correlation functions $u_p(t_p\cdots t_1)$ in all possible ways, and the summation is extended over all possible products. We shall use the convention that the times within a u function are for $t>0$ ordered so that the earlier times stand to the left and later times stand to the right in successive order, and for $t<0$ we shall prescribe the opposite ordering. This is the same rule as that used for $\langle v_\kappa(t_p)\cdots v_\kappa(t_1)\rangle_T$.

n_p shall denote the number of times the function u_p appears in a product. We can thus characterize a product by the partition $(n_2,n_4,\cdots)$. All products corresponding to the same partition can be obtained from one of the products by simply permuting the times involved. To conserve the number of t's appearing in each product one evidently has

$$p_1n_{p_1}+p_2n_{p_2}+\cdots=2n. \tag{43}$$

When using Eq. (42) in Eq. (39) and considering $t\rightarrow\infty$, the major contribution to each integral comes from the term in which (t_1,t_2), (t_3,t_4), etc., are taken together. This allows the distance in time between all the pairs to be large but the times within a pair have to be close together, how close being determined by the rapidity with which $u_2(t_2,t_1)\rightarrow 0$ as $|t_2-t_1|\rightarrow\infty$. All the other terms in (42) contribute to a lower power of t.

For $t\rightarrow 0$, on the other hand, the integrals in (39) are given by the values of $\langle v_\kappa^{2n}\rangle_T$, which for a Maxwellian distribution of the velocity can be written

$$[(2n)!/2^n n!](\langle v_\kappa^2\rangle_T)^n. \tag{44}$$

Exactly the same results is obtained by using (42) and assuming that all the u_{2p}, $p>1$, vanish. In fact, by neglecting these correlation functions one obtains the "Gaussian approximation" given in Eqs. (16) and (17). From the arguments above, we would expect this approximation to be good either when the scattering cross section depends entirely on the behavior of the system over a very short period of time or when the behavior for large times plays a dominant role. One might hope that the same approximation should be reasonably good for intermediate values of time as well.

We shall proceed by taking into account the higher correlation functions also and thus get the corrections to the Gaussian approximation. First, we notice that the number of products in (42) corresponding to a given partition is[26]

$$N(n_2,n_4,n_6,\cdots) =(2n)!/(2!)^{n_2}n_2!(4!)^{n_4}n_4!(6!)^{n_6}n_6!\cdots. \tag{45}$$

The integrations in (39) can be simplified considerably so that a partial summation of the series is possible. To show this it is convenient to extend the time region within which the velocity correlation functions have been used so far, namely $t_{2n}\leqslant t_{2n-1}\leqslant\cdots\leqslant t_1\leqslant t$ for $t>0$ and $t_{2n}\geqslant t_{2n-1}\geqslant\cdots\geqslant t_1\geqslant t$ for $t<0$. We introduce a new set of functions $f_p(t_p,\cdots t_1)$ such that

$$f_p(t_p,\cdots t_1)=u_p(t_p,\cdots t_1), \tag{46}$$

in the regions mentioned above and define them to be invariant for permutations of the times $(t_p,\cdots t_1)$. Using (42), it follows that

$$\begin{aligned}\int_0^t dt_1\int_0^{t_1}dt_2\cdots\int_0^{t_{2n-1}}dt_{2n}\,\langle v_\kappa(t_{2n})\cdots v_\kappa(t_1)\rangle_T &=\int_0^t dt_1\int_0^{t_1}dt_2\cdots\int_0^{t_{2n-1}}dt_{2n}\sum(f_{p1}\cdots f_{p1})\cdots\\ &\qquad\times(f_{p_\nu}\cdots f_{p_\nu})\\ &=\frac{1}{(2n)!}\int_0^t dt_1\cdots\int_0^t dt_{2n}\sum(f_{p1}\cdots f_{p1})\cdots\\ &\qquad\times(f_{p_\nu}\cdots f_{p_\nu}).\end{aligned}\tag{47}$$

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[26] To indicate how one arrives at (45) let us consider Eq. (41). In the first curly bracket, we have taken all products of u_2 functions which correspond to the partition $(3,0,\cdots)$. By permuting the times involved in a product we get 6! terms. However, permutations leading only to a re-ordering of the u_2 functions should not be counted. We thus get 6!/3! different permutations. Due to our convention of time ordering in each u function, we have also to discard any permutation of the times inside the u functions. This leads to another denominator $(2!)^3$.

In the second curly bracket, all terms corresponding to the partition $(1,1,0,\cdots)$ are included. The total number of permutations is 6!, and we have to divide this number by 2!, the number of permutations inside u_2; and by 4!, the number of permutations inside u_4.

Each product belonging to the same partition now gives an equal contribution to the integral. We shall introduce a shorter notation $\gamma_p(t)$ for the basic quantities as follows:

$$\gamma_p(t)=\frac{1}{(2p)!}\int_0^t dt_1\cdots\int_0^t dt_{2p}\, f_{2p}(t_{2p},\cdots t_1)$$
$$=\int_0^t dt_1\int_0^{t_1} dt_2\cdots\int_0^{t_{2p-1}} dt_{2p}\, u_{2p}(t_{2p},\cdots t_1). \tag{48}$$

Using (45) and (47) in Eq. (39), $\langle A(t)\rangle_T$ can be brought into the following form:

$$\langle A(t)\rangle_T=\sum_{n_2=0}^{\infty}\sum_{n_4=0}^{\infty}\cdots\left\{\frac{1}{n_2!}(-\kappa^2\gamma_1)^{n_2}\right\}\left\{\frac{1}{n_4!}(\kappa^4\gamma_2)^{n_4}\right\}\cdots$$
$$=\exp\left\{\sum_{n=1}^{\infty}(-\kappa^2)^n\gamma_n(t)\right\}. \tag{49}$$

The first term in the series in the exponential gives the Gaussian approximation mentioned above. An alternative expression for the first few γ_n is given below and is obtained in a straightforward manner from the definition of the u_{2n} functions.

$$\gamma_1(t)=\int_0^t dt_1\int_0^{t_1} dt_2\,\langle v_\kappa(t_2)v_\kappa(t_1)\rangle_T$$
$$\gamma_2(t)=\int_0^t dt_1\int_0^{t_1} dt_2\cdots\int_0^{t_3} dt_4\,\langle v_\kappa(t_4)\cdots v_\kappa(t_1)\rangle_T -\tfrac{1}{2}[\gamma_1(t)]^2, \tag{50}$$
$$\gamma_3(t)=\int_0^t dt_1\int_0^{t_1} dt_2\cdots\int_0^{t_5} dt_6\,\langle v_\kappa(t_6)\cdots v_\kappa(t_1)\rangle_T -\gamma_1(t)\gamma_2(t)-\tfrac{1}{6}[\gamma_1(t)]^3.$$

[Later we shall redefine $\gamma_1(t)$ to include a term $(-i\hbar t/2M)$.]

We could have obtained these functions in a simpler way by expanding the right-hand side of Eq. (49) in powers of κ^2 and comparing it with expression (39) term by term. In fact such an attempt has been made before.[6] We have preferred to use the above procedure because some essential properties of the γ_n functions are then revealed more clearly.

It is not possible to calculate $\gamma_n(t)$ without a more detailed knowledge of the correlation functions involved. However, some important properties do not depend on the particular choice of the system. For instance, using the property

$$u_{2n}(t_{2n}+t,\cdots,t_1+t)=u_{2n}(t_{2n},\cdots,t_1), \tag{51}$$

and introducing a new set of time variables

$$\begin{aligned} t_1'&=t_1-t_{2n},\\ t_2'&=t_2-t_{2n},\\ &\cdots\\ t_{2n-1}'&=t_{2n-1}-t_{2n},\\ t_{2n}'&=t_{2n}, \end{aligned} \tag{52}$$

one time integration can be carried out. We get

$$\gamma_n(t)=\int_0^t dt_1\cdots\int_0^{t_{2n-1}} dt_{2n} \times u_{2n}(0,\,t_{2n-1}-t_{2n},\cdots,t_1-t_{2n})$$
$$=\int_0^t dt_1'\int_0^{t'_1} dt_2'\cdots\int_0^{t'_{2n-2}} dt'_{2n-1} \times\int_0^{t-t_1'} dt_{2n}'\, u_{2n}(0,\,t_{2n-1}',\cdots,t_1')$$
$$=\int_0^t (t-t_1')dt_1'\left\{\int_0^{t_1'} dt_2'\cdots \times\int_0^{t_{2n-2}'} dt_{2n-1}'\, u_{2n}(0,t_{2n-1}',\cdots,t_1')\right\}. \tag{53}$$

$u_{2n}(0,t_{2n-1}',\cdots,t_1')\rightarrow 0$ for $|t_1'|\rightarrow\infty$ and it seems reasonable to assume that the decrease in its magnitude for increasing time is rapid enough to make the following quantities converge.

$$D_n=\int_0^\infty dt_1'\int_0^{t_1'} dt_2'\cdots \times\int_0^{t_{2n-2}'} dt_{2n-1}'\, u_{2n}(0,t_{2n-1}',\cdots,t_1'),$$
$$C_n=\int_0^\infty t_1'dt_1'\int_0^{t_1'} dt_2'\cdots \times\int_0^{t_{2n-2}'} dt_{2n-1}'\, u_{2n}(0,t_{2n-1}',\cdots,t_1'). \tag{54}$$

It then follows from (53) that

$$\gamma_n(t)\rightarrow D_nt-C_n, \tag{55}$$

for $t\rightarrow\infty$, and since $F(\boldsymbol{\kappa},t)$ is the complex conjugate of $F(\boldsymbol{\kappa},-t)$ we get

$$\gamma_n(t)\rightarrow D_n^*|t|-C_n^* \tag{56}$$

for $t\rightarrow-\infty$.

For small times we can directly expand $\gamma_n(t)$ in a power series in t using (48) and the definition of u_{2n}. Thus we get

$$\gamma_n(t)\rightarrow u_{2n}(0,0,\cdots,0)t^{2n}/(2n)! \tag{57}$$

for $t\rightarrow 0$.

In special cases, of course, some of the constants above may vanish. For instance, all $u_{2n}(0,0,\cdots,0)$ for $n>1$ are zero if the velocity distribution function is Maxwellian. This is always true for a classical system, if the interaction is velocity independent, and as shown in Landau and Lifshitz (see earlier reference) it is also true if the quantum corrections up to order $\hbar^2$ are included. According to Schofield[6] $\gamma_2(t)$ starts in a classical treatment as t^8, whereas in the same treatment $\gamma_1(t)$ starts as t^2. This can be seen from Eq. (50) without much difficulty.

If we use the expression for $\langle A(t)\rangle_T$ given in Eq. (49) together with the term $j=0$ in Eq. (9) we get for $S_{\text{inc}}(\boldsymbol{\kappa},\omega)$ the following

$$S_{\text{inc}}(\boldsymbol{\kappa},\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-i\omega t}\exp\{\sum_{n=1}^{\infty}(-\kappa^2)^n\gamma_n(t)\}dt, \quad (58)$$

where for $n\geqslant 2$, $\gamma_n(t)$ are defined in (48) and in an alternative way in (50). $\gamma_1(t)$ is re-defined to include the factor $\exp(i\hbar t\kappa^2/2M)$ in Eq. (9). Henceforth the notation $\gamma_1(t)$ will stand for

$$\gamma_1(t)=-i(\hbar t/2M)+\int_0^t (t-t_1)\langle v_\kappa(0)v_\kappa(t_1)\rangle_T dt_1, \quad (59)$$

which for an isotropic system can also be written in the form given in Eq. (17). Hence D_1, introduced in Eq. (54), shall be redefined as

$$D_1=-i(\hbar/2M)+\int_0^\infty \langle v_\kappa(0)v_\kappa(t_1)\rangle_T dt_1. \quad (60)$$

Using the fact that $F_s(\boldsymbol{\kappa},t+i\beta)$ is real, and hence that $\gamma_n(t+i\beta)$ is real, we immediately conclude that all D_n are real and that

$$\text{Im}C_n=\beta D_n;\quad \beta=\hbar/2k_BT. \quad (61)$$

D_1 can be shown to be the diffusion constant.

The result obtained in Eqs. (55) and (56) for large times may seem to contradict what was said earlier, namely that the Gaussian approximation should be good both for small and for large times. It is certainly true that $\langle A(t)\rangle_T$ does not in general go over into the expression (15) when $|t|\rightarrow\infty$. However, we are not directly interested in $\langle A(t)\rangle_T$ or $F_s(\boldsymbol{\kappa},t)$ but in its Fourier transform $S_{\text{inc}}(\boldsymbol{\kappa},\omega)$. To reach experimentally the time region where (55) or (56) is valid κ must be chosen small and consequently the non-Gaussian contribution will be negligible. To see this more clearly let us first estimate the order of magnitude of D_n. We get from the definitions in (54)

$$|D_n|\lesssim(\langle v_\kappa^2\rangle_T)^n\tau_n^{2n-1}, \quad (62)$$

where τ_n is the time region within which u_{2n} is different from zero. Assuming that τ_n's are all of the same order of magnitude we have for $|t|$ large

$$\sum_{n=1}^{\infty}(-\kappa^2)^n\gamma_n(t)\sim-\kappa^2D_1|t|$$
$$\times\{1+d_2\kappa^2\langle v_\kappa^2\rangle_T\tau_1^2+d_4\kappa^4\langle v_\kappa^4\rangle_T\tau_1^4+\cdots\}, \quad (63)$$

where d_n are constants of order unity or lower. It is obvious that to have the main contribution to the integral in (58) from a time region $t>\tau_1$ the value of κ must be such that $\kappa^2D_1\tau_1\approx\kappa^2\langle v_\kappa^2\rangle_T\tau_1^2\ll 1$ in which case the non-Gaussian part in Eq. (63) is small. Here we have made the assumption that the infinite series behaves properly; it should be positive for all values of κ and be of the order unity or higher. This certainly has not been proved and remains an assumption.

It is of interest to see whether Van Hove's $G_s(\mathbf{r},t)$ function tends to a Gaussian form in $\mathbf{r}$ when $|t|\rightarrow\infty$. We therefore write

$$G_s(\mathbf{r},t)=(2\pi)^{-3}\int\exp(-i\boldsymbol{\kappa}\cdot\mathbf{r})\exp[-\kappa^2\gamma_1(t)]$$
$$\times\exp[\sum_{n=2}^{\infty}(-\kappa^2)^n\gamma_n(t)]d\boldsymbol{\kappa}. \quad (64)$$

Let us for the sake of simplicity consider the first order correction to the Gaussian approximation. Expanding the second exponential in (64) and retaining only the first two terms, we get

$$G_s(\mathbf{r},t)=(2\pi)^{-3}\int\exp(-i\boldsymbol{\kappa}\cdot\mathbf{r})$$
$$\times\exp[-\kappa^2\gamma_1(t)]\{1+\kappa^4\gamma_2(t)+\cdots\}d\boldsymbol{\kappa}$$
$$=[4\pi\gamma_1(t)]^{-\frac{3}{2}}\exp[-r^2/4\gamma_1(t)]$$
$$\times\{1+[\gamma_2(t)/\gamma_1(t)^2]((15/4)-5[r^2/4\gamma_1(t)]$$
$$+[r^2/4\gamma_1(t)]^2)+\cdots\}. \quad (65)$$

For $|t|\rightarrow\infty$ the correction term tends to

$$(D_2/D_1^2|t|)[(15/4)-5(r^2/4D_1|t|)$$
$$+(r^2/4D_1|t|)^2]. \quad (66)$$

Thus for the region of interest, namely where $r^2/4D_1|t|$ is not too large, the correction term tends to zero for large times as $1/|t|$. The higher order corrections decrease even more rapidly. From the estimate in (62) it is now obvious that after a certain time the function $G_s(\mathbf{r},t)$ is Gaussian and satisfies the simple diffusion equation, and that in order of magnitude τ is the same as the relaxation time of the velocity autocorrelation function $\langle\mathbf{v}(0)\cdot\mathbf{v}(t)\rangle_T$. Experiments on some simple liquids have given for τ a value of the order 10^{-11} to 10^{-12} sec.

In spite of the fact that $F_s(\boldsymbol{\kappa},t)$ tends to a Gaussian form for $t\rightarrow 0$, this approximation is not in general valid for $S_{\text{inc}}(\boldsymbol{\kappa},\omega)$ for $\kappa\rightarrow\infty$. This is clearly seen from

Eq. (58) after making a change of integration variable, $y=\kappa t$, and expanding the γ_n functions in powers of y. We can write

$$S_{\mathrm{inc}}(\boldsymbol{\kappa},\omega)=\frac{1}{2\pi\kappa}\int_{-\infty}^{\infty}\exp[-iy(\omega-\omega_R)/\kappa]$$
$$\times\exp\{\sum_{n=1}^{\infty}g_n(y)\}dy, \quad (67)$$

where

$$g_1(y)=-(y^2/2)\langle v_\kappa{}^2\rangle_T+O(1/\kappa),$$
$$g_2(y)=(y^4/24)[\langle v_\kappa{}^4\rangle_T-3(\langle v_\kappa{}^2\rangle_T)^2]+O(1/\kappa),\ \text{etc.,} \quad (68)$$

and $\omega_R=\hbar\kappa^2/2M$.

The g_n's for $n>1$, obviously do not tend to zero for $\kappa\rightarrow\infty$ if the velocity distribution is non-Maxwellian. However, as mentioned earlier the distribution is Maxwellian even if quantum corrections up to order $\hbar^2$ are taken care of. We can, therefore, expect the correction to be extremely small except for very low temperatures.

We shall end this section by considering a system where the velocity of an atom can be considered as a superposition of a large number of components $\dot{\xi}_s(t)$, which are dynamically independent. Each component is supposed to give a contribution of order $N^{-\frac{1}{2}}$, N being the number of components. We can thus write

$$v_\kappa(t)=N^{-\frac{1}{2}}\textstyle\sum_s\dot{\xi}_s(t). \quad (69)$$

This condition is exactly fulfilled for a solid in the harmonic approximation.

The velocity autocorrelation function is given by

$$\langle v_\kappa(t_2)v_\kappa(t_1)\rangle_T=N^{-1}\textstyle\sum_s\langle\dot{\xi}_s(t_2)\dot{\xi}_s(t_1)\rangle_T. \quad (70)$$

For $u_4(t_4,\cdots,t_1)$ we get

$$u_4(t_4,\cdots,t_1)=N^{-2}\textstyle\sum_s\{\langle\dot{\xi}_s(t_4)\cdots\dot{\xi}_s(t_1)\rangle_T$$
$$-\langle\dot{\xi}_s(t_4)\dot{\xi}_s(t_3)\rangle_T\langle\dot{\xi}_s(t_2)\dot{\xi}_s(t_1)\rangle_T-\cdots\}, \quad (71)$$

and similar expressions for the higher correlation functions. This leads to

$$\gamma_2(t)=O(1/N),\quad \gamma_3(t)=O(1/N^2),\ \text{etc.,} \quad (72)$$

and hence they can be neglected if N is large, a result which is also a consequence of the central limit theorem.

We have in this way proved the Gaussian form of $F_s(\boldsymbol{\kappa},t)$ for a harmonic solid without explicitly making use of the particular properties of the eigenstates. If we had done that we would, in fact, have found that $\gamma_n(t)$ for $n>1$ vanish exactly independent of the value of N.

If the anharmonic effects are not too large, one might expect that the functions $\gamma_n(t)$ decrease rapidly in magnitude for increasing values of n. It would, in fact, be interesting if one could test the Gaussian approximation for a solid by measuring the κ dependence of the Debye-Waller factor at high temperatures. According to Eq. (58), it should have a form

$$\exp\{-\sum_{n=1}^{\infty}(-\kappa^2)^nC_n\}, \quad (73)$$

where C_n's are the same constants as in Eq. (55); diffusion having been neglected all D_n must vanish and all C_n are real.

In the case of a liquid, the anharmonic effects are certainly large but here new phenomena such as diffusion are responsible for giving more randomness to the motion. This may have a decreasing effect on γ_n for $n>1$. It is important to try to estimate the magnitude of the non-Gaussian correction. The effect is most clearly revealed by plotting $\ln F_s(\boldsymbol{\kappa},t)$ vs κ^2 and determining how much the curve deviates from a straight line. Such an analysis has been made by Egelstaff[15] using the experimental data of Brockhouse and Pope[27] for liquid lead.

VI. GAUSSIAN APPROXIMATION

In most computations made so far, the Gaussian approximation has been made. An argument in favor of this is that it is known to hold exactly in certain special cases: a harmonic solid, an ideal gas and a system for which the motion of the atoms is governed by Langevin's equation; it seems reasonable to make the the same approximation for other systems as well. This is particularly attractive since the interpretation of the experimental data is considerably simplified.

We shall discuss the Gaussian approximation in greater detail starting from the expression given in Eqs. (16) and (17). We have seen that in this approximation the scattering is completely determined by the function

$$\gamma_1(t)=-i\hbar t/2M+\tfrac{1}{3}\int_0^t(t-t_1)\langle\mathbf{v}(0)\cdot\mathbf{v}(t_1)\rangle_T dt_1. \quad (74)$$

To satisfy the fluctuation-dissipation theorem we use the formulation in Eq. (22) with

$$H_s(\boldsymbol{\kappa},t)=\exp[-\kappa^2\rho(t)], \quad (75)$$

where $\rho(t)=\gamma_1(t+i\beta)$.

As it stands $\rho(t)$ is not in a very convenient form and we will therefore bring it into a form, more suitable for direct application. For that purpose we first consider the second derivative

$$d^2\rho(t)/dt^2=d^2\gamma_1(t+i\beta)/dt^2=\tfrac{1}{3}\langle\mathbf{v}(0)\cdot\mathbf{v}(t+i\beta)\rangle_T. \quad (76)$$

By making use of the dissipation-fluctuation theorem [Eq. (21)] we can replace $\langle\mathbf{v}(0)\cdot\mathbf{v}(t)\rangle_T$ by its real part and after integration we get

$$\rho(t)=\rho(0)+\frac{1}{3}\int_0^t(t-t_1)\sec\left(\beta\frac{d}{dt_1}\right)$$
$$\times\mathrm{Re}\langle\mathbf{v}(0)\cdot\mathbf{v}(t_1)\rangle_T dt_1. \quad (77)$$

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[27] B. N. Brockhouse and N. K. Pope, Phys. Rev. Letters 3, 259 (1959).

As mentioned earlier, $\rho(t)$ is an even function of t and hence no linear term in t should appear in (77).

The constant $\rho(0)$ is obtained by making use of the reality of $\rho(0)$ and the fluctuation-dissipation theorem [Eq. (19)]. Denoting the differential operator d/dt by D, we have

$$\begin{aligned}\rho(0)&=\gamma_1(i\beta)=\exp(i\beta D)\gamma_1(0)\\ &=\cos(\beta D)\ \mathrm{Re}\gamma_1(0)-\sin(\beta D)\ \mathrm{Im}\gamma_1(0)\\ &=-\beta\left\{\frac{d}{dt}\ \mathrm{Im}\gamma_1(t)\right\}_{t=0}+\beta^2\left\{\frac{\cos(\beta D)-1}{\beta^2D^2}\left[\frac{d^2}{dt^2}\ \mathrm{Re}\gamma_1(t)\right]_{t=0}-\frac{\sin(\beta D)-\beta D}{\beta^2D^2}\left[\frac{d^2}{dt^2}\ \mathrm{Im}\gamma_1(t)\right]_{t=0}\right\}\\ &=\frac{\hbar^2}{4Mk_BT}+\beta^2\left\{\frac{\cos(\beta D)-1}{\beta^2D^2}+\frac{\sin(\beta D)-\beta D}{\beta^2D^2}\tan(\beta D)\right\}\mathrm{Re}\langle\mathbf{v}(0)\cdot\mathbf{v}(t)\rangle_{T/t=0}.\end{aligned}\qquad(78)$$

For sufficiently high temperatures we can expand $\rho(0)$ in powers of $1/T$ giving

$$\rho(0)=\frac{\hbar^2}{8Mk_BT}\left\{1-\frac{\hbar^2M\langle a^2\rangle_T}{48k_B{}^3T^3}+\cdots\right\},\qquad(79)$$

where $\langle a^2\rangle_T$ is the mean-square acceleration of a particle. The second term above can be estimated. Assuming $\langle a^2\rangle_T$ to be the same as for a Debye solid with a Debye temperature θ one can easily show that

$$\hbar^2M\langle a^2\rangle_T/48k_B{}^3T^3=\tfrac{1}{5}(\theta/4T)^2.\qquad(80)$$

This is certainly very small compared to unity for any reasonable values of θ for a liquid, except possibly liquid neon and argon.

If we retain only the first term in Eq. (79) and the first term in the expansion of the differential operator in (77) and further if we replace $\mathrm{Re}\langle\mathbf{v}(0)\cdot\mathbf{v}(t)\rangle_T$ by its classical analog $\langle\mathbf{v}(0)\cdot\mathbf{v}(t)\rangle_{\mathrm{cl}}$, we obtain an expression which was suggested in an earlier paper.[19,28]

$$\rho(t)=\frac{\hbar^2}{8Mk_BT}+\frac{1}{3}\int_0^t(t-t_1)\langle\mathbf{v}(0)\cdot\mathbf{v}(t_1)\rangle_{\mathrm{cl}}dt_1.\qquad(81)$$

For a solid, the approximations suggested for the integral in Eq. (77) imply retaining only the first term in the expansion

$$\frac{1}{\sin(\beta\omega)}=\frac{1}{\beta\omega}(1-\tfrac{1}{6}\beta^2\omega^2+\cdots),\qquad(82)$$

where ω is a phonon frequency. We can neglect the quantum correction whenever $\theta^2/24T^2\ll1$. The smallness of this term for temperatures higher than the Debye temperature indicates that we should be able to neglect completely the quantum corrections for most liquids. We, therefore, except Eq. (81) to be a good approximation for most liquids.

The problem thus reduces to that of calculating $\langle\mathbf{v}(0)\cdot\mathbf{v}(t)\rangle_{\mathrm{cl}}$ based on Newton's equation. One approach would be to solve these equations directly for a large number of particles. This, of course, requires a high speed computer, but it now seems feasible. Another approach would be to assume a certain form for the autocorrelation function with some adjustable parameters and try to fit the calculated scattering cross section to the experimental data.

VII. SPECTRAL REPRESENTATION OF $\gamma_1(t)$

In analogy with the case of a solid, Egelstaff *et al.*[29] have suggested the introduction of a frequency spectrum for a liquid; this spectrum being that of the velocity autocorrelation function. Here we shall show how this can be done in a natural way without any reference to a solid.

We define two frequency spectra related to the real and imaginary parts of the velocity correlation function:

$$\mathrm{Im}\langle\mathbf{v}(0)\cdot\mathbf{v}(t)\rangle_T=\frac{3\hbar}{2M}\int_0^\infty\omega f(\omega)\sin(\omega t)d\omega,\qquad(83)$$

$$\mathrm{Re}\langle\mathbf{v}(0)\cdot\mathbf{v}(t)\rangle_T=\frac{3\hbar}{2M\beta}\int_0^\infty g(\omega)\cos(\omega t)d\omega.\qquad(84)$$

From the fluctuation-dissipation theorem (Eq. 19) it now follows that

$$g(\omega)=\beta\omega\coth(\beta\omega)f(\omega).\qquad(85)$$

The integral of $f(\omega)$ can be evaluated by integrating both sides of Eq. (83). The right-hand side gives

$$\frac{3\hbar}{2M}\int_0^\infty dt\int_0^\infty\omega f(\omega)\sin(\omega t)d\omega=\frac{3\hbar}{2M}\int_0^\infty f(\omega)d\omega,$$

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[28] By definition $\rho(t)$ here differs from that in reference 19 by a factor two.

[29] P. Egelstaff, S. J. Cocking, R. J. Royston, and I. M. Thorson, Proc. Symposium on Slow Neutron Scattering, International Atomic Energy Agency, Vienna, 1960, paper IS, p. 10.

and the integration of the left-hand side leads to

$$\begin{aligned}\int_0^\infty \mathrm{Im}\langle \mathbf{v}(0)\cdot\mathbf{v}(t)\rangle_T dt &= \frac{1}{2i}\int_0^\infty \{\langle[v_x(0);v_x(t)]\rangle_T+\cdots\}dt\\ &=(1/2i)\{\langle[v_x(0);r_x(\infty)]\rangle_T\\ &\quad-\langle[v_x(0);r_x(0)]\rangle_T+\cdots\},\\ &=3\hbar/2M,\end{aligned}$$

v_x, v_y, v_z are the three Cartesian components of $\mathbf{v}$ and r_x, r_y, r_z are the corresponding components of the position vector; and where commutation rules for position and velocity operators have been used.

We thus have

$$\int_0^\infty f(\omega)d\omega=1. \tag{86}$$

Using the above spectral representation in Eq. (74), it can easily be shown that

$$\gamma_1(t)=\frac{\hbar}{2M}\int_0^\infty \frac{f(\omega)}{\omega}\times\{\coth(\beta\omega)[1-\cos(\omega t)]-i\sin(\omega t)\}d\omega. \tag{87}$$

This is exactly the same expression as obtained earlier for a harmonic solid.[30] We thus see that this particular form for $\gamma_1(t)$ is not a consequence of the harmonic nature of the motion but purely a consequence of the fluctuation-dissipation theorem. The system is here characterized by a velocity spectrum $f(\omega)$, which in the case of a harmonic solid is identical with the frequency distributions of the normal modes.

For $\rho(t)$ we get the form which has been used by Egelstaff and Schofield in a recent paper[31]

$$\rho(t)=\frac{\hbar}{2M}\int_0^\infty \frac{f(\omega)}{\omega}\tanh(\beta\omega/2)d\omega+\frac{\hbar}{2M}\int_0^\infty \frac{f(\omega)}{\omega\sinh(\beta\omega)}[1-\cos(\omega t)]d\omega. \tag{88}$$

Again, if we approximate $\tanh(\beta\omega/2)$ by $\beta\omega/2$ we arrive at the first term in Eq. (79).

As shown by Egelstaff *et al.* the value of $f(0)$ is uniquely determined by the diffusion constant. We can see this easily by inverting the Fourier transforms in Eqs. (83) and (84):

$$f(\omega)=\frac{4M}{3\pi\hbar}\frac{1}{\omega}\int_0^\infty \mathrm{Im}\langle\mathbf{v}(0)\cdot\mathbf{v}(t)\rangle_T\sin(\omega t)dt \tag{89}$$

$$=\frac{4M}{3\pi\hbar}\frac{\tanh(\beta\omega)}{\omega}\int_0^\infty \mathrm{Re}\langle\mathbf{v}(0)\cdot\mathbf{v}(t)\rangle_T\cos(\omega t)dt. \tag{90}$$

Since the diffusion constant D is given by

$$D=\frac{1}{3}\int \mathrm{Re}\langle\mathbf{v}(0)\cdot\mathbf{v}(t)\rangle_T dt. \tag{91}$$

We get

$$f(0)=2MD/\pi k_BT. \tag{92}$$

If we assume that $\langle\mathbf{v}(0)\cdot\mathbf{v}(t)\rangle_T$ decreases rapidly enough for $t\rightarrow\infty$, we can conclude from Eq. (89) that $f(\omega)$ can be expanded in powers of ω^2

$$f(\omega)=2MD/\pi k_BT+c_2\omega^2+c_4\omega^4+\cdots, \tag{93}$$

where

$$c_{2n}=\frac{4M}{3\pi\hbar}\frac{(-1)^n}{(2n+1)!}\int_0^\infty t^{2n+1}\,\mathrm{Im}\langle\mathbf{v}(0)\cdot\mathbf{v}(t)\rangle_T dt. \tag{94}$$

Assuming $\langle\mathbf{v}(0)\cdot\mathbf{v}(t)\rangle_T$ to have all its time derivatives continuous everywhere and tending to zero for $t\rightarrow\pm\infty$, we also conclude from Eq. (89) that $f(\omega)$ decreases more rapidly than any power of $1/\omega$ for $\omega\rightarrow\infty$.

GENERAL REMARKS

In the present investigation, we have covered in detail only a part of the scattering problem. For instance, no attempt has been made to calculate or even estimate the non-Gaussian contribution to the scattering. Furthermore, we feel that a better approximation for the coherent correction is needed in order to be able to analyze the experimental data in greater detail However, in the calculation of the incoherent scattering cross section in the Gaussian approximation one requires a knowledge of the velocity autocorrelation function only. The classical autocorrelation function has been calculated on the basis of a simple model of a liquid, and these results are reported in the following paper.

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[30] See A. Sjölander, Arkiv Fysik **14**, 315 (1958).

[31] P. A. Engelstaff and P. Schofield, Nuclear Sci. and Eng. **12**, 260, (1962).