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CORRELATIONS IN LIQUIDS AND APPLICATIONS
TO SLOW NEUTRON SCATTERING

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Correlations in Liquids and Applications
to Slow Neutron Scattering*

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ABSTRACT

Correlation functions for liquids in general, and the scattering function in particular, are studied. The Langevin noise-source theory is used in conjunction with the conventional, linearized hydrodynamic equations. Calculations are initially carried out without resorting to long wavelength approximations in the Markoffian limit. Agreement with earlier results for the description of light scattering is obtained. Investigation of neutron scattering leads to the striking prediction that central peak half-widths are independent of momentum transfer and inversely proportional to viscosity—but independent of thermal diffusivity, at least for some liquids. Some experimental evidence in favor of this result is presented. The theory is then substantially generalized by relaxing the assumption of Markoffian behavior. Generalizations of Einstein's relation between the mobility and diffusion matrices and Onsager's relations are obtained. Generalized formulas for correlation functions and for the scattering function are presented. It is suggested that the generalized theory provides a supplementary (to kinetic theory) path for the exploration of limitations and extensions of the equations employed in the present study.

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I. INTRODUCTION

In this paper we examine the applicability of a particular, but conventional,⁽¹⁾ mathematical description of fluctuations in liquids to the interpretation of slow neutron scattering by normal liquids. The description alluded to consists of the familiar linearized, hydrodynamic equations for the density, momentum, and temperature. However, we prefer not to refer to the present study as a hydrodynamical theory of fluctuations, but rather to refer to it as a configuration space theory (to distinguish it from kinetic theory which is couched in phase space). The reason for this is that any reference to hydrodynamics seems to imply automatically severe restrictions, e.g., results valid only for long times and long wavelengths. But, of course, any given configuration space description of a particular system is merely an approximation to a more elaborate description; and, at least in principle, the more elaborate description can be made as exact as desired in any given case. In fact, it will be at least a part of the burden of this work to suggest an avenue along which the search for such elaboration may be conveniently, and perhaps fruitfully, explored.

We choose to initiate the study in the context of the conventional description for several reasons. First of all, to our knowledge, it has not been done before. Kadanoff and Martin⁽²⁾ have discussed fluctuations in liquids in the context of precisely the same description, but limited their exploration of its implications to long wavelengths, which rendered their explicit results

inapplicable to a study of neutron scattering. Subsequently, Mountain⁽³⁾ studied exactly the same problem that interests us here, i.e., the calculation of the scattering function, using exactly the same equations that we will use. But his primary motivation was the interpretation of light-scattering measurements, so he too made use of long wavelength approximations. His results were essentially the same as Kadanoff and Martin's and hence were similarly not applicable to the study of neutron scattering. Recently, light-scattering experiments have been reported^(4,5) which are in good agreement with the predictions of Refs. (2) and (3). Also, Felderhof⁽⁶⁾ has employed a similar description of liquids in a study of critical opalescence. Some of his analysis is in close parallel to our discussion in Section II. However, here again, explicit results are obtained and discussed in the long wavelength (light scattering) limit.

Secondly, an exact calculation of the scattering function is quite feasible using the conventional equations, and leads to a formula that is analytically tractable. These results can be compared (in a sense to be discussed in detail later) with some of the data for neutron scattering by liquid lead reported by Randolph and Singwi,⁽⁷⁾ and appear to be in significant agreement therewith. Included in this agreement is a confirmation of an unexpected prediction of the theory that the width of the central peak of the scattered spectrum is independent of momentum transfer and of thermal conductivity, but instead depends inversely on the viscosity of the liquid. As will be discussed in greater detail later, the sense in which the experiment reveals widths independent of momentum transfer requires some explanation.

For $k = |\underline{p}-\underline{p}'|/\hbar \simeq 2 \times 10^8 \text{ cm}^{-1}$, the widths exhibit a marked decrease, presumably related to diffraction effects.⁽⁸⁾ But, for $k \gtrsim 3 \times 10^8 \text{ cm}^{-1}$, the widths appear to remain fairly constant. It is this latter, constant width that we correlate with the theoretical prediction. This is in striking contrast to the situation for light scattering, as seen from our results as well as from those of Refs. (2) and (3). In the latter instance, the width of the central peak is proportional to the thermal conductivity and to the square of the momentum transfer. Furthermore, it appears from comparison with the data on lead scattering, that the conventional description does not begin to break down seriously until nearly the limits of energy transfer accessible to measurement. As will be shown, the first step in the direction of generalization of the theory provides a qualitative correction to this defect at the high energy transfer (short time) limit, and points a way toward still greater refinement.

A third reason for pressing this issue is that these equations may be more justified in the application to fluctuation theory than their derivation from the hydrodynamic equations by linearization would imply. This possibility is suggested by two considerations. For small displacements from thermal equilibrium, the fluctuation-dissipation theorem provides a fairly strong, independent (of macroscopic hydrodynamical considerations) argument⁽²⁾ in favor of using linearized equations for mean values to describe fluctuating quantities. And secondly there does not appear to be available now, or in the near future, an analytical demonstration of the precise limits of validity of any given mathematical description of fluctuations. Consequently, we feel

that the conventional mathematical model should be explored to the full and tested, where possible, against measurement. Then, if found wanting, it should not be discarded, but rather built upon in ways indicated by the microscopic, configuration-space theories^(9,10) and by stochastic arguments developed elsewhere⁽¹¹⁾ and applied here.

In Section II, we present the equations to be used in the present application and obtain their solutions appropriate to the calculation of various correlation functions. In Section III, we apply the solution for the density-density correlation function to an interpretation of measurements of the scattering of slow neutrons by normal liquids. In Section IV, we discuss ways of elaborating the present theory employing stochastic arguments.

II. CALCULATION OF CORRELATION FUNCTIONS

Since the mathematical model to be used here is entirely familiar,⁽¹⁾ we merely present it without further comment, i.e.,

$$\frac{\partial \rho}{\partial t} + \rho_0 U = 0, \quad (1a)$$

$$\rho_0 \frac{\partial U}{\partial t} + \frac{c_0^2}{\gamma} \nabla^2 \rho + \frac{c_0^2 \beta \rho_0}{\gamma} \nabla^2 T - \eta \nabla^2 U = 0, \quad (1b)$$

$$\rho_0 c_v \frac{\partial T}{\partial t} + \frac{c_v(\gamma-1)\rho_0}{\beta} U - \lambda \nabla^2 T = 0. \quad (1c)$$

Here we have introduced ρ , $U \equiv \underline{\nabla} \cdot \underline{W}$, and T to represent the space and time dependent mass density, divergence of mean velocity, and temperature respectively. Using the subscript, o , to designate equilibrium values, these quantities are small in the sense that ρ/ρ_0 and T/T_0 are small compared to unity, and (as will be seen later) that $U/C_0 k$ is also small compared to one, where C_0 is the speed of sound and k is the reciprocal of the wavelength characteristic of the disturbances to be examined. The remaining parameters are:

$\gamma = C_p/C_v$ where C_p and C_v are the specific heats at constant pressure and volume respectively; $\beta =$ cubical coefficient of thermal expansion; $\eta \equiv (\frac{4}{3} \eta_s + \eta_b)$, η_s and η_b being the shear and bulk viscosities; and $\lambda =$ thermal conductivity.

It is convenient to space-Fourier transform these equations and introduce dimensionless dependent variables according to

$$\psi_1(\underline{k}, t) \equiv \rho/\rho_0, \quad (2a)$$

$$\psi_2(\underline{k}, t) \equiv U/C_0 k, \quad (2b)$$

$$\psi_3(\underline{k}, t) \equiv T/T_0 . \quad (2c)$$

We then obtain the matrix equation

$$\frac{\partial \Psi}{\partial t} + M\Psi = 0 \quad (3a)$$

where

$$\Psi \equiv \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \end{pmatrix} \quad (3b)$$

and

$$M = C_0 k \begin{pmatrix} 0 & 1 & 0 \\ -\frac{1}{\gamma} & Z & -\frac{\beta T_0}{\gamma} \\ 0 & \frac{\gamma-1}{\beta T_0} & y \end{pmatrix} . \quad (3c)$$

The new parameters introduced into the matrix M are Mountain's "small quantities," i.e., $Z = \eta k / \rho_0 C_0$ and $y = \lambda k / \rho_0 C_0 C_V$. These parameters are indeed small in the case of light scattering ($k \simeq 10^5 \text{ cm}^{-1}$), being of the order of 10^{-2} or less. However, for the neutron scattering case ($k \simeq 10^8 \text{ cm}^{-1}$) they are large, i.e., ~ 10 and $\sim 10^3$ respectively for lead. Thus we will obtain correlation functions in general and the scattering function in particular without further approximation.

We shall base our correlation analysis on the Langevin noise-source approach which has been presented elsewhere in detail. The advantages and flexibility of this approach for fluctuation analysis in general have been discussed and demonstrated by M. Lax in a series of papers. (12,13)

In this approach one adds a noise source to the matrix equation (3), describing the mean evolution of the physical system, to account for the fluctua-

tions of the dynamical variables about their equilibrium values:

$$\frac{\partial \Psi}{\partial t} + M\Psi = Q \quad (4)$$

where Q is a column vector with components $Q_1(\underline{k}, t)$, $Q_2(\underline{k}, t)$ and $Q_3(\underline{k}, t)$. We shall assign the proper statistical properties to the noise source—more precisely, to its correlation matrix—at various stages in the analysis to facilitate successive levels of approximation.

We now define a time-dependent correlation matrix as

$$\Lambda(\underline{k}, t) \equiv \langle \Psi(-\underline{k}, 0) \tilde{\Psi}(\underline{k}, t) \rangle_{\mathbb{T}} , \quad (5)$$

where $\tilde{\Psi}$ is the transpose of Ψ , $\langle \rangle_{\mathbb{T}}$ means thermal average, and we have explicitly noted that Λ depends only on the magnitude of \underline{k} . The (1,1)-element of this matrix is the density-density correlation function required for the calculation of the scattering function. Solving Eq. (3) and its transpose, we find that

$$\Lambda(\underline{k}, t) = \int_0^\infty dx \int_0^\infty dy e^{-Mx} \langle Q(-\underline{k}, -x) \tilde{Q}(\underline{k}, t-y) \rangle_{\mathbb{T}} e^{-\tilde{M}y} . \quad (6)$$

At this point we make our first assumption about the unknown quantity, Q , i.e.,

$$\langle Q(-\underline{k}, t) \tilde{Q}(\underline{k}, t') \rangle_{\mathbb{T}} = \delta(t-t') D(\underline{k}) , \quad (7)$$

where $D(\underline{k})$ is called the diffusion matrix. It can be shown that the assumption embodied in Eq. (7) is equivalent to the assumption that the time evolution of Ψ is Markoffian.^(11,13) In Section IV we will examine some of the significance and consequences of relaxing this assumption. Entering (7) into

(6), we find that

$$\begin{aligned}\Lambda(k,t) &= \Lambda(k,0)e^{-\tilde{M}t}, \quad t > 0 \\ &= e^{-M|t|} \Lambda(k,0), \quad t < 0 ,\end{aligned}\quad (8)$$

where $\Lambda(k,0)$ is the static correlation matrix. In deriving Eq. (8) we have used

$$\Lambda(k,0) = \int_0^\infty dy e^{-My} D(k) e^{-\tilde{M}y}, \quad (9)$$

which can be solved to obtain

$$D(k) = M\Lambda(k,0) + \Lambda(k,0)\tilde{M}. \quad (10)$$

This is known as the generalized Einstein relation. (11)

Introducing (7) into (6) and taking the time Fourier transform, we obtain (using (10)),

$$\begin{aligned}\Lambda(k,\omega) &= \int_{-\infty}^{\infty} dt e^{-i\omega t} \Lambda(k,t) \\ &= 2\text{Re}(M-i\omega I)^{-1} \Lambda(k,0).\end{aligned}\quad (11)$$

Evidently the desired density-density correlation function, $\Lambda_{11}(k,\omega)$, depends upon $\Lambda_{11}(k,0)$, $\Lambda_{21}(k,0)$, and $\Lambda_{31}(k,0)$ which are the static density-density, velocity-density, and temperature-density correlation functions respectively. However, in the present instance, time reversibility⁽¹⁴⁾ requires $\Lambda_{21}(k,0)$ and Λ_{23} to be zero (note that the static correlation matrix is symmetric). This is readily shown from the fact that time reversibility requires that

$$\Lambda_{ij}(k,t) = \epsilon_i \epsilon_j \Lambda_{ij}(k,-t), \quad (12)$$

where $\epsilon_i = \pm 1$ depending on whether ψ_i is even or odd under time reversal (ψ_1 and ψ_3 are even, and ψ_2 is odd since it is essentially a velocity). Evaluating (12) at $t = 0$ implies that

$$\Lambda_{ij}(k,0)(1-\epsilon_i\epsilon_j) = 0, \quad (13)$$

which leads immediately to the conclusion noted above.

Because of the particular character of the matrix, M (and hence because of the level of development of configuration space theory that we are using here) we can show that $\Lambda_{31}(k,0)$ is also equal to zero. Using (12) together with Eq. (8), we find that

$$\Lambda(k,0)_{im}(e^{-Mt})_{jm} = \epsilon_i\epsilon_j(e^{-Mt})_{im}\Lambda(k,0)_{mj}, \quad (14)$$

which is satisfied for all t if, in addition to (13),

$$\Lambda(k,0)_{im}M_{jm} = \epsilon_i\epsilon_jM_{im}\Lambda(k,0)_{mj}. \quad (15)$$

The latter are the Onsager relations.⁽¹⁴⁾ Evaluating (15) for $i = 1$ and $j = 3$ we obtain

$$M_{12}\Lambda_{23} = M_{32}\Lambda_{12} + M_{33}\Lambda_{13}. \quad (16)$$

Since $\Lambda_{12} = \Lambda_{23} = 0$, we conclude that Λ_{13} , the static density-temperature correlation function is also zero—in accordance with an assertion by Mountain.⁽³⁾

We note in passing that this last result depends explicitly on Eq. (8) which holds only for Markoffian systems. We return to this point later.

It appears from the foregoing discussions that the static correlation matrix $\Lambda(k,0)$ is diagonal with the diagonal elements $\Lambda_{jj} = \langle \psi_j(k,0)\psi_j(k,0) \rangle_T$. We may note for completeness that the Onsager's relations (15) enable one to express the static velocity-velocity and temperature-temperature correlation function in terms of the static density-density correlation function by considering the special cases $i = 1, j = 2$, and $i = 2, j = 3$. The results are

$$\langle \psi_2(k,0)\psi_2(k,0) \rangle_T = \frac{1}{\gamma} \langle \psi_1(k,0)\psi_1(k,0) \rangle_T \quad (17a)$$

$$\langle \psi_3(k,0)\psi_3(k,0) \rangle_T = \frac{\gamma-1}{\gamma^2} \langle \psi_1(k,0)\psi_1(k,0) \rangle_T \quad (17b)$$

The diffusion matrix D defined by (7) can now be evaluated explicitly using the generalized Einstein's relation (10). Substituting M from (4c) into (10) we find that D is also a diagonal matrix with the diagonal elements

$$D_{11} = 0$$

$$D_{22} = 2 \frac{C_0 k Z}{\gamma} \langle \psi_1(k,0)\psi_1(k,0) \rangle_T \quad (18a)$$

$$D_{33} = 2C_0 k y \frac{\gamma-1}{\gamma^2} \langle \psi_1(k,0)\psi_1(k,0) \rangle_T \quad (18b)$$

Since $D_{11} = 0$ we may conclude, with the help of (7), that $\langle Q_1(-\underline{k},t)Q_1(\underline{k},t) \rangle = 0$, and hence $Q_1(\underline{k},t) \equiv 0$. This implies that the continuity relation $(\partial\rho/\partial t) + \rho_0 U = 0$ does not contain any random driving force, i.e., the continuity relation is true for the instantaneous values as well as the mean values of $Q(\underline{k},t)$ and $U(\underline{k},t)$, at the present level of approximation.

We may also conclude that the random forces $Q_2(\underline{k},t)$ and $Q_3(\underline{k},t)$ in the

momentum and temperature equations are uncorrelated, i.e., $\langle Q_2(-\underline{k}, t)$

$Q_3(\underline{k}, t') \rangle = 0$, because $D_{23} = D_{32} = 0$.

III. APPLICATION TO THE CALCULATION OF THE NEUTRON SCATTERING FUNCTION

Here we apply the results of the preceding sections to an attempt at a quantitative interpretation of the scattering of slow neutrons by normal liquids—specifically the measurements of Randolph and Singwi for liquid lead.⁽⁷⁾ To this end, we recall the relation between the scattering cross-section and the scattering function—the latter being closely related to the density-density correlation function studied above, i.e.,

$$\sigma(k,\omega) = \sqrt{\frac{E'}{E}} \sigma_0 S(k,\omega) , \quad (19)$$

where E and E' are the energies of the incident and scattered neutrons, σ_0 is the neutron-nuclear cross-section, and where now

$$\begin{aligned} \underline{k} &= (\underline{p}-\underline{p}')/\hbar , \\ \omega &= (E-E')/\hbar , \end{aligned} \quad (20)$$

are the momentum and energy transfer variables. The scattering function is defined to be

$$S(k,\omega) \equiv \frac{1}{2\pi N} \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle n(-\underline{k},0)n(\underline{k},t) \rangle_T . \quad (21)$$

Here, N is the number of atoms in the scattering sample, and again we have explicitly noted that the scattering function depends upon the magnitude of k only. The operator $n(\underline{k},t)$ represents the number density in the liquid and is related to $\rho(\underline{x},t)$ by

$$\rho(\underline{x}, t) = mn(\underline{x}, t) .$$

Observing that

$$S(k, -\omega) = e^{-\hbar\omega/\theta} S(k, \omega) , \quad (22)$$

we define a symmetrized scattering function by

$$\begin{aligned} G(k, \omega) &\equiv \pi N [S(k, \omega) + S(k, -\omega)] \\ &= \frac{1}{2} \int dt e^{-i\omega t} \langle [n(-\underline{k}, 0), n(\underline{k}, t)]_+ \rangle_{\mathbb{T}} , \end{aligned} \quad (23)$$

where $[]_+$ means anti-commutator. Using Eq. (22), we then find that

$$S(k, \omega) = \frac{e^{\hbar\omega/2\theta}}{\pi N} \operatorname{Sech} \frac{\hbar\omega}{2\theta} G(k, \omega) . \quad (24)$$

It is the quantity, G , that we will calculate by the classical arguments discussed above.

Classically we have

$$\begin{aligned} &\langle [n(-\underline{k}, 0), n(\underline{k}, t)]_+ \rangle_{\mathbb{T}} \\ &= 2 \langle n(-\underline{k}, 0) n(\underline{k}, t) \rangle_{\mathbb{T}} \\ &= 2 \int d^3x' d^3x e^{i\underline{k} \cdot (\underline{x} - \underline{x}')} \langle n(\underline{x}', 0) n(\underline{x}, t) \rangle_{\mathbb{T}} . \end{aligned} \quad (25)$$

But

$$\begin{aligned} &\langle n(\underline{x}', 0) n(\underline{x}, t) \rangle_{\mathbb{T}} \\ &= \frac{1}{m^2} \langle \rho(\underline{x}', 0) \rho(\underline{x}, t) \rangle_{\mathbb{T}} \\ &= n_{\mathbb{T}}^2 \langle \psi_1(\underline{x}', 0) \psi_1(\underline{x}, t) \rangle_{\mathbb{T}} , \end{aligned} \quad (26)$$

so that our symmetrized scattering function becomes

$$G(k, \omega) = n_{\mathbb{T}}^2 \Lambda_{11}(k, \omega) . \quad (27)$$

It is now merely a straightforward, though lengthy, manipulation to obtain

$$G(k, \omega) = \frac{ga_1 \hbar}{\theta} \frac{1+a_2 x^2}{(1-a_3 x^2)^2 + x^2 (a_4 - a_5 x^2)^2} . \quad (28)$$

In this formula we have introduced the notations

$$\begin{aligned} g &= \langle n(-\underline{k}, 0) n(\underline{k}, 0) \rangle_{\mathbb{T}} , \\ a_1 &= [\gamma(1+Zy)-1]/y , \\ a_2 &= \epsilon^2 Z/y [Zy+(\gamma-1)/\gamma] , \\ a_3 &= \gamma \epsilon^2 (1+Z/y) , \\ a_4 &= \gamma \epsilon Z (1+1/yZ) , \\ a_5 &= \gamma \epsilon^3 /y , \\ \epsilon &= \theta / \hbar C_0 k , \\ x &= \hbar \omega / \theta . \end{aligned} \quad (29)$$

It is important to compare this formula with the one obtained by Mountain.⁽³⁾ His solutions were tailored for light scattering. In such cases, $k \simeq 10^5 \text{ cm}^{-1}$ and hence y and Z are usually of the order of 10^{-2} . Furthermore, in the experiment reported by Lastovka and Benedek,⁽⁴⁾ the range of x was $\lesssim 10^{-9}$. Under these circumstances, $a_2 x^2$, $a_3 x^2$, and $a_5 x^2$ are all negligible. Hence the scattering function reduces to

$$G(k, \omega) \rightarrow \frac{ga_1 \hbar}{\theta} \frac{1}{1+a_4^2 x^2}, \quad (30)$$

which predicts a half-width, in frequency space, for the central peak given

by

$$\frac{1}{a_4} \frac{\theta}{\hbar} \approx \frac{\lambda k^2}{\rho_0 c_p}. \quad (31)$$

This formula was verified in the experiment referred to above. The main point here is that the half-width is proportional to the thermal conductivity and to the square of the momentum transfer.

A strikingly different result obtains for the half-width in the event of neutron scattering. In this instance, $k \gtrsim 10^8$, and the parameters y and Z are of the order of 10^3 and 10 respectively for some liquids such as lead and sodium. Here also the half-width is approximatable by (i.e., liquid lead and sodium),

$$\begin{aligned} \frac{\theta}{\hbar} \frac{1}{a_4} &= \frac{\theta}{\hbar \gamma \epsilon Z} \left(1 + \frac{1}{yZ}\right)^{-1} \\ &\approx \frac{\theta}{\hbar \gamma \epsilon Z} = \frac{\rho_0 c_0^2}{\gamma \eta}. \end{aligned} \quad (32)$$

Interesting points of comparison between (31) and (32) are that the relatively high momentum transfer neutron-scattering measurements appear to be characterized by central peak half-widths which are independent of (or at least insensitive to; for (32) is, after all, approximate; and recall the earlier remarks about diffraction narrowing) momentum transfer and thermal conductivity; but conversely may be sensitive to viscosity.

Of course the formula (28) for the scattering function is hardly explicit with respect to momentum transfer because of the factor, $g = \langle n(\underline{-k}, \omega) n(\underline{k}, \omega) \rangle_T$. A separate calculation of this static density-density correlation function will obviously, ultimately be required for the interpretation of angular distribution experiments. However Randolph's measurements yield a substantial amount of data for energy transfer at constant momentum transfer—sufficient indeed to provide a rather interesting test of the theory at the present level. Hence quantitative comparison with experiment will be with Eq. (28) in which $k = |\underline{p} - \underline{p}'|/\hbar$ enters merely as another parameter. Actually, over most of the range of the lead scattering data (excepting the range of momentum transfers characterized by diffraction narrowing), Eq. (30) is just as good with a_4 given in Eq. (32).

In Fig. 1 we have plotted the widths of the symmetrized scattering function ($G(k, \omega)$ vs. ω for constant k) as a function of k . The effect of diffraction narrowing is clearly discernible—the minimum occurring at about $k = 2.1 \times 10^8 \text{ cm}^{-1}$. Above $k = 3 \times 10^8 \text{ cm}^{-1}$ it is seen that the widths are nearly constant. Using for this constant value, $x = .035$, we calculate for $a_4 = \gamma \epsilon Z$ a value of 28.6. Thus $\eta = 28.6 \rho_0 C_0^2 / \gamma \theta = 7.4 \times 10^{-2}$ poise; employing $C_0 = 1.77 \times 10^5 \text{ cm/sec}$, $\gamma = 1.1$, $\rho_0 = 10.6 \text{ gm/cm}^3$, and $\theta = 8.63 \times 10^{-14} \text{ ergs}$. The shear viscosity has been independently determined to be 2.58×10^{-2} poise, which implies a bulk viscosity, $\eta_b = \eta - \frac{4}{3} \eta_s$, of 4.0×10^{-2} poise.

In Fig. 2, we present a few graphs of the formula

$$G(k, \omega) = G_0 / (1 + a_4^2 x^2), \quad (33)$$

for comparison with experiment. The curves have been roughly fitted to all the data rather than depending on normalization at a given point. It seems that the agreement is quite good. However, it is seen that near the end of the range of large energy transfers, the theory invariably predicts too much scattering. We argue that this apparent systematic discrepancy at large energy transfers is indicative of a breakdown of the Markoffian assumption implied by Eq. (7). In the next section, we show how relaxation of this assumption can lead to qualitative correction of this discrepancy.

IV. GENERALIZATION OF THE THEORY

The explicit form of Eq. (28) used for the above discussion of the half-width of the central peak depends considerably upon the Markoffian assumption implied in Eq. (7). Because of the narrowness of these peaks the half-widths are determined in the region of small energy transfer—hence by the long time behavior of the liquid. Also, we have seen some indication that the short time behavior (region of large energy transfers) is not adequately dealt with in the analysis so far.

In recognition of this difficulty, we now introduce a non-Markoffian description of liquid correlations by replacing Eq. (7) by

$$\langle Q(-\underline{k}, t) \tilde{Q}(\underline{k}, t') \rangle_T = f(t-t')D(k), \quad (34)$$

where now f is an even function of the time which vanishes rapidly as $|t-t'|$ becomes large compared to memory times, and D is a new realization of the diffusion matrix. Though an explicit form for f is not needed for most of the subsequent analysis, it is convenient to think of it as

$$f(t) = \frac{e^{-t^2/2\tau^2}}{\tau\sqrt{2\pi}}, \quad (35)$$

where τ is to be appropriately chosen. Evidently, with this choice, we recapture the previous results in the limit as τ (the memory time) goes to zero.

The expression for the correlation matrix, Eq. (6), now becomes

$$\Lambda(t) = \int_0^\infty dx \int_0^\infty dy e^{-Mx} D e^{-\tilde{M}y} f(t+x-y). \quad (36)$$

For compactness we no longer explicitly note the k-dependence of Λ, D , and M . In order to find $\Lambda(t)$ in terms of $\Lambda(o)$, we must solve the following matrix equation for D , i.e.,

$$\Lambda(o) = \int_0^\infty dx \int_0^\infty dy e^{-xM} D e^{-y\tilde{M}} f(x-y). \quad (37)$$

We rewrite Eq. (37) as

$$e^{Mt} \Lambda(o) e^{\tilde{M}t} = \int_{-\infty}^t dx \int_{-\infty}^t dy e^{xM} D e^{y\tilde{M}} f(x-y), \quad (38)$$

and differentiate to obtain

$$M\Lambda(o) + \Lambda(o)\tilde{M} = D\tilde{X} + XD, \quad (39)$$

where we have defined the matrix

$$X = \int_0^\infty dx f(x) e^{-xM}. \quad (40)$$

Equation (39) is now modified to read

$$e^{Xt} (M\Lambda(o) + \Lambda(o)\tilde{M}) e^{\tilde{X}t} = \frac{d}{dt} [e^{Xt} D e^{\tilde{X}t}], \quad (41)$$

and is then integrated from $-\infty$ to t to obtain

$$D = M\Gamma(o) + \Gamma(o)\tilde{M}, \quad (42)$$

with the identification,

$$\Gamma(o) = \int_0^\infty dx e^{-xX} \Lambda(o) e^{-x\tilde{X}}. \quad (43)$$

Equation (42) for D is of the same form as Eq. (10), and represents a generalization of Einstein's relation between the diffusion matrix and the mobility matrix, M , to non-Markoffian processes. The matrix, Γ , which replaces Λ in Eq. (10) will be called the modified static correlation matrix. Many of the results of the preceding sections will retain their form in the non-Markoffian description with a simple replacement of $\Lambda(0)$ by $\Gamma(0)$.

Substituting (42) into (36) leads to

$$\Lambda(t) = \int_0^\infty dx [f(t+x)e^{-xM} \Gamma(0) + \Gamma(0)e^{-x\tilde{M}} f(t-x)] . \quad (44)$$

This equation describes the time dependence of the dynamic correlation matrix in the non-Markoffian case, and reduces to (8) when $f(t)$ is a delta function. The symmetrized scattering function is now calculated from the Fourier transform of Λ_{11} (recall Eqs. (11) and (27)), i.e.,

$$G(k, \omega) = 2n_T^2 F(\omega) \text{Re}[(M - i\omega I)_{1j}^{-1} \Gamma_{j1}(0)] , \quad (45)$$

where $F(\omega)$ is the Fourier transform of $f(t)$.

We turn now to the task of determining the modified static correlation matrix, Γ . Again we make use of the requirement of time reversibility expressed in Eq. (12). Entering (44) into (12) we obtain

$$\int_0^\infty dx [f(t+x) - \epsilon_i \epsilon_j f(t-x)] [(e^{-xM} \Gamma(0))_{ij} - \epsilon_i \epsilon_j (\Gamma(0) e^{-x\tilde{M}})_{ij}] = 0 , \quad (46)$$

which will be satisfied for all t if

$$(e^{-xM} \Gamma(0))_{ij} = \epsilon_i \epsilon_j (\Gamma(0) e^{-x\tilde{M}})_{ij} \quad (47)$$

holds for all x . But, as noted earlier (Eqs. (12) and (15)), Eq. (47) is satisfied if

$$\Gamma(o)_{ij} = \epsilon_i \epsilon_j \Gamma(o)_{ij} , \quad (48a)$$

$$(M\Gamma(o))_{ij} = \epsilon_i \epsilon_j (\Gamma(o)\tilde{M})_{ij} \quad (48b)$$

are satisfied. Hence Onsager's relations in the non-Markoffian case are the same for the modified static correlation matrix as for the unmodified static correlation matrix in the Markoffian case. Thus, as before

$$\Gamma(o)_{ij} = 0, \quad i \neq j , \quad (49a)$$

$$\Gamma(o)_{22} = \frac{1}{\gamma} \Gamma(o)_{11} , \quad (49b)$$

$$\Gamma(o)_{33} = \frac{\gamma-1}{\gamma^2} \Gamma(o)_{11} . \quad (49c)$$

Formula (44), together with the definition (40), can now be used to relate the modified and unmodified static correlation matrices, i.e.,

$$\Lambda(o) = X\Gamma(o) + \Gamma(o)\tilde{X} . \quad (50)$$

Inverting, we find that

$$\Gamma(o)_{11} = (2X_{11})^{-1} \Lambda(o)_{11} , \quad (51a)$$

$$\Gamma(o)_{22} = (2X_{22})^{-1} \Lambda(o)_{22} , \quad (51b)$$

$$\Gamma(o)_{33} = (2X_{33})^{-1} \Lambda(o)_{33} . \quad (51c)$$

Also from (50), we find that

$$\Lambda(o)_{13} = X_{13}\Gamma(o)_{33} + \Gamma(o)_{11}X_{31} = 2\Gamma(o)_{33}X_{13} \quad (52)$$

which is no longer zero as it was in the Markoffian case. In fact, from Eqs. (51) we see that the relations among the diagonal elements of $\Lambda(o)$ have been changed by the non-Markoffian description. Clearly $\Lambda(o)_{12} = \Lambda(o)_{21} = 0$ according to time reversibility as discussed earlier, and as can be seen from Eq. (50) after a little manipulation.

It is interesting to note at this point that the diffusion matrix is also diagonal in the non-Markoffian description of the liquid, as can be seen by substituting (43) into (42). The diagonal elements are $D_{11} = 0$, $D_{22} = M_{22}\Gamma(o)_{22}$ and $D_{33} = M_{33}\Gamma(o)_{33}$. Since $D_{11} = 0$, we again conclude that the noise source in the continuity equation, i.e., $Q_1(\underline{k}, t)$, is identically zero. This observation leads to an interesting relation between the second moment of the symmetrized scattering law $G(k, \omega)$ and the static density-density correlation function. Using the relation between the auto-correlation function of random process and its derivative, we find from (1a)

$$\rho_o^2 \langle U(o)U(t) \rangle = - \frac{\partial^2}{\partial t^2} \langle \rho(o)\rho(t) \rangle .$$

If we evaluate this relation at $t = 0$, and express $\langle \rho(o)\rho(t) \rangle$ in terms of $G(k, \omega)$ we get

$$\int_{-\infty}^{+\infty} G(k, \omega) \omega^2 d\omega = (C_o k)^2 \Lambda(o)_{22} .$$

We can express $\Lambda(o)_{22}$ in terms of $\Lambda(o)_{11}$ using (49) and (51) and finally obtain

$$\int_{-\infty}^{+\infty} G(k,\omega)\omega^2 d\omega = \frac{c_0^2 k^2}{\gamma} \frac{X_{22}}{X_{11}} g \quad (53)$$

where X_{11} and X_{22} are to be obtained from (40).

Entering (51a) into (45), we calculate the symmetrized scattering function to be

$$G(k,\omega) = g \frac{F(\omega)L(\omega)}{\int_{-\infty}^{\infty} d\omega F(\omega)L(\omega)}, \quad (54)$$

where

$$L(\omega) = \text{Re}[(M-i\omega I)_{11}^{-1}], \quad (55)$$

and $g(k)$ has been defined earlier in Eq. (29). We note that the integral of $G(k,\omega)$ over all ω is proportional to g as required.

Formula (54) is, we believe, a new result for the symmetrized scattering function for liquids. Because of its complexity (even given the explicit form (35) for the memory function), and because we know of no experimental results to test the explicitly non-Markoffian aspects of it, we have not explored it quantitatively. However, one or two qualitative features are worth noting in conclusion. Both formula (54), and the one obtained earlier in the Markoffian limit, Eq. (28), exhibit the characteristic form of the convolution approximation—this in spite of the fact that there was no attempt to deal separately with the "self" and "distinct" scattering functions. Furthermore, even the elementary Markoffian result was seen to be in substantial agreement with observation over a large range of momentum transfers. Light scattering at low momentum transfer verifies the dependence of half-widths on k^2 and thermal

diffusivity; whereas neutron scattering at high momentum transfer appeared to be in significant agreement with the prediction that the half-width is (above the region of diffraction narrowing) in this case, independent of momentum transfer and depends on viscosity instead of thermal diffusivity. We suggest therefore that possibly the path outlined above might be a fruitful one along which to press an investigation of the implications and range of validity of the convolution approximation.

Another observation is based on the use of the formula (35) for the memory function. Its Fourier transform is

$$F(\omega) = e^{-\omega^2 \tau^2 / 2} . \quad (56)$$

Suppose now we estimate values for the transport parameters, η and λ , from calculations in gas phase; and take a limit to the ideal gas by letting collision cross-sections approach zero. We then find that Z and y approach infinity, and hence further that $L(\omega)$ approaches zero like Z^{-1} . In this limit, the symmetrized scattering function simply becomes

$$\begin{aligned} G(k, \omega) &\rightarrow gF(\omega) / \int_{-\infty}^{\infty} d\omega F(\omega) \\ &= \frac{g\tau e^{-\omega^2 \tau^2 / 2}}{\sqrt{2\pi}} . \end{aligned} \quad (57)$$

For the truly ideal gas we would require $\tau = (m/\theta k^2)^{-1/2} = (v_{T1}k)^{-1}$. For a dilute, real gas, we might choose instead, $\tau^2 = (v_{T1}k)^{-2} + \tau_c^2$, where τ_c is a collision time, i.e., the effective radius of an atom divided by the thermal speed of the atoms. It is interesting to note that both of these characteristic times generalize naturally to the liquid phase. The collision time retains

its meaning in the liquid, whereas $(v_T k)^{-1} \rightarrow (C_0 k)^{-1}$, i.e., the time required for a sound signal to travel the characteristic distance, k^{-1} . Thus we suggest for the memory function appearing in Eq. (54) the form

$$F(\omega) = e^{-\frac{\omega^2}{2} (\tau_c^2 + 1/C_0^2 k^2)} \quad (58)$$

Whichever of these memory times is the larger will dominate in any given case. In any event, for sufficiently large momentum transfers, the collision time will dominate since it is probably not sensitive to k in this limit. In the lead scattering case, for $k = 3 \times 10^8 \text{ cm}^{-1}$, $(C_0 k)^{-1} = 1.8 \times 10^{-14} \text{ sec}$. If we estimate τ_c as R/v_T , where R is the radius of a lead atom taken to be approximately 10^{-8} cm , and v_T is the thermal speed of the atoms, i.e., $v_T \simeq 2 \times 10^4 \text{ cm/sec}$; we find, $\tau_c \simeq 5 \times 10^{-13} \text{ sec}$. Thus, quite possibly, the dominant memory time in the high momentum transfer range of the lead scattering data is the collision time. Indeed it is observed in Fig. 2 that the break point corresponding to τ_c (cf. the curve for $k = 4$ for example) is about $x = 0.15$ which yields $\tau_c = 1.2 \times 10^{-13} \text{ sec}$.

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FIGURE CAPTIONS

Fig. 1. Central peak half-widths of half maximum as a function of momentum transfer. The circled points are taken from Fig. 2.

Fig. 2. The symmetrized scattering function vs. energy transfer for constant k . The solid lines are theoretical, and represent graphical fitting of the experimental data to the formula $(1+a\frac{2}{4}x^2)^{-1}$. Circles, crosses, squares, and triangles are measured values taken from enlargements of figures presented in Ref. (7) supplied us by Randolph. Note the systematic deviation of theory (Markoffian) from experiment for large energy transfers.

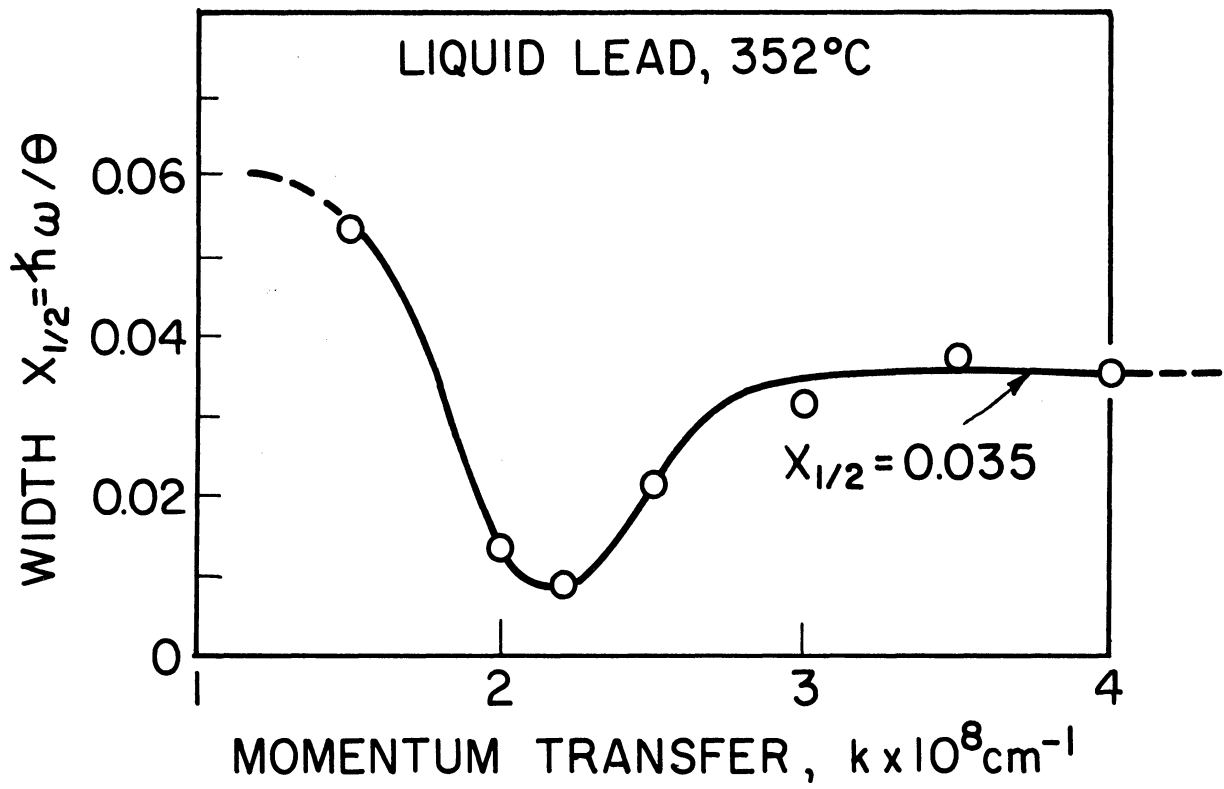


Fig. 1.

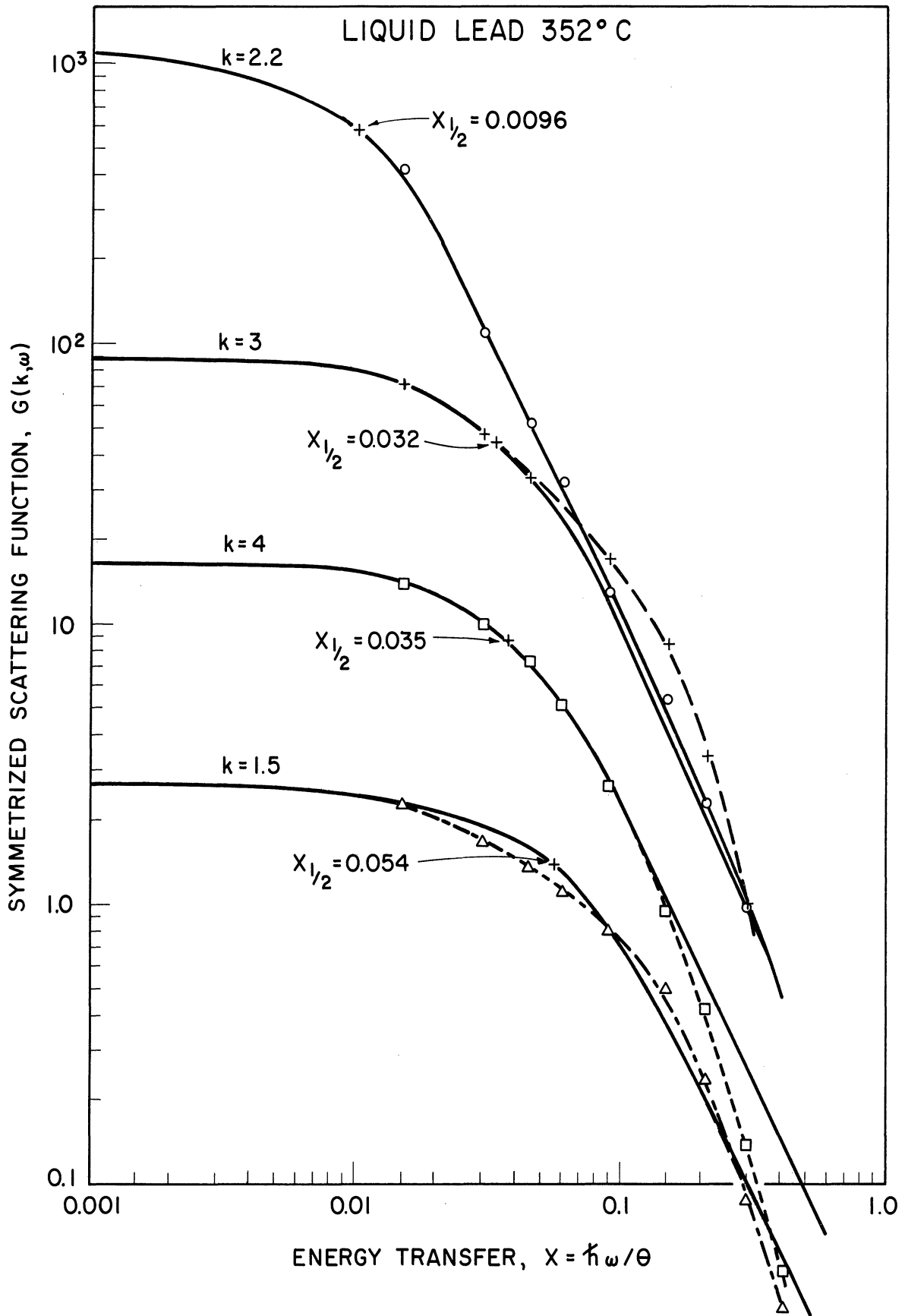


Fig. 2.

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