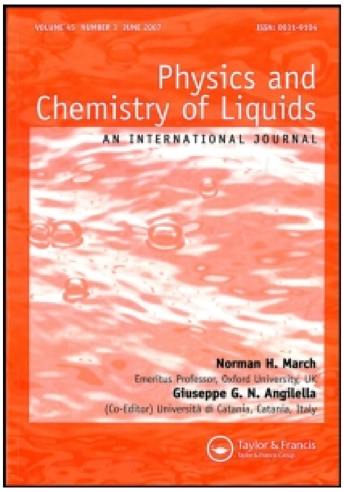
This article was downloaded by:
On: *28 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Self-motion response and incoherent scattering function in classical liquids

A. A. Kugler[a]
[a] Institut Max von Laue-Paul Langevin, Cedex 156, 38-Grenoble-Gare, France

To cite this Article Kugler, A. A.(1972) 'Self-motion response and incoherent scattering function in classical liquids', Physics and Chemistry of Liquids, 3: 4, 205 — 223

To link to this Article: DOI: 10.1080/00319107208084100

URL: http://dx.doi.org/10.1080/00319107208084100

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Physics and Chemistry of Liquids. 1972. Vol. 3, pp. 205–223

Self-motion Response and Incoherent Scattering Function in Classical Liquids

A. A. KUGLER

Institut Max von Laue–Paul Langevin
Cedex 156
38–Grenoble-Gare/France

Abstract—The self-motion response function and incoherent scattering function $S_s(k, \omega)$ for simple classical liquids is studied using an exact representation presented in a previous paper. The latter can be termed a generalized mean field representation to distinguish it from the generalized hydrodynamic representation introduced elsewhere. It is shown that the present formalism offers a natural and convenient way of relating the experimentally determined $S_s(k, \omega)$ to some basic quantities involving only the interaction. Using a small part of the recent experimental data on incoherent neutron scattering in liquid argon, we are able to calculate $S_s(k, \omega)$ and other quantities of interest and to compare with the rest of the data.

1. Introduction

In a separate paper$^{(1)}$ (hereafter referred to as I) we have introduced an exact representation for the density–density response function of simple liquids. This representation has been termed a generalized mean field representation since it is based on the usual expression for the response function except that the static, effective potential is replaced by one which is both wave number and frequency dependent. The formalism allowed us to analyze recent data on inelastic scattering of neutrons from liquid argon$^{(2)}$ and to calculate the van Hove coherent scattering function starting from some exact formulae.

In this paper we use the same method as in I to discuss a similar representation for the self-motion response function $\chi_s(k, z)$ and incoherent scattering function $S_s(k, \omega)$. These functions describe the dynamic phenomena in the liquid associated with the motion of one selected (test) particle. Intuitively we expect that these functions will have a simpler structure than the corresponding functions discussed in I which describe the density fluctuations associated with the correlated motions of many particles.

Let us emphasize at the outset that the method discussed here is quite different from the generalized hydrodynamic representation introduced originally by Kadanoff and Martin.$^{(3,4)}$ Although both representations are exact and describe the same response function, the emphasis and method of application differ somewhat. Hence these representations should be regarded as providing complementary frameworks for the description of the same physical phenomena.

Single-particle motion in simple classical liquids has already been the subject of numerous theoretical investigations as well as some molecular dynamics calculations.$^{(5,6)}$ Here we do not intend to review or appraise the various methods of approach to the problem but refer to the recent works of Levesque, Verlet$^{(6)}$ and Desai$^{(7)}$ for extensive discussion, summary and references to previous work on this subject.

The self-motion response function $\chi_s(k, z)$ from which the incoherent scattering function $S_s(k, \omega)$ as well as the velocity autocorrelation function can be derived is defined as follows: if an external potential $u_s(\mathbf{r}, t)$ is coupled only to the selected test particle at $\mathbf{r}_s(t)$ through the corresponding density $\rho_s(\mathbf{r}, t) = \delta(\mathbf{r} - \mathbf{r}_s(t))$, then the change in ρ_s from its value $1/V$ (where V is the volume of the system) is given in terms of its Fourier components by

$$\langle \rho_s(\mathbf{k}, \omega) \rangle = -\frac{1}{N} \chi_s(k, \omega + i\epsilon)\, u_s(\mathbf{k}, \omega), \tag{1.1}$$

where N is the number of particles in the system and ϵ is a positive infinitesimal.

In Sec. 2 we review the basic relations, analytic properties and sum rules connected with the response function $\chi_s(k, \omega + i\epsilon)$ and its imaginary part, $\chi_s''(k, \omega)$; the latter is related in a trivial fashion to $S_s(k, \omega)$. In Sec. 3 we discuss an exact mean field representation for $\chi_s(k, z)$ of the form

$$\chi_s(k, z) = \frac{\chi_0(k, z)}{1 + \phi_s(k, z) \chi_0(k, z)}, \tag{1.2}$$

where $\chi_0(k, z)$ is the response function for an ideal gas, and the complex effective potential $\phi_s(k, z)$ describes all the " memory " effects arising from the interaction between the selected particle and the other particles in the liquid. This potential vanishes when the interaction is switched off; then (1.2) gives automatically the correct result for an ideal gas. We discuss the analytic properties of $\phi_s(k, z)$ and show that it can be obtained from its imaginary part, $\phi_s''(k, \omega)$, which thus forms the basic unknown of this theory and contains all the information about the dynamics of the single-particle motion. Also given in Sec. 3 are some exact formulae relating the incoherent scattering function $S_s(k, \omega)$ to $\phi_s''(k, \omega)$. It is shown that there is a particularly simple, exact relation between $S_s(k, \omega = 0)$ and ϕ_s'', which is useful in the interpretation of experimental data(2) on $S_s(k, \omega)$. The last part of Sec. 3 contains some simple but formally exact expressions for the self-diffusion constant.

In Sec. 4 we use two simple ansatz forms for $\phi_s''(k, \omega)$ in which the basic parameter, a relaxation time, is determined from the experimental data on $S_s(k, \omega = 0)$, making use of an exact relation referred to above. With these forms for $\phi_s''(k, \omega)$ we have calculated $S_s(k, \omega)$, finding excellent agreement with the experimentally determined $S_s(k, \omega)$ for liquid argon.(2) Finally, the relation of the above forms for $\phi_s''(k, \omega)$ to previous model calculations of the velocity autocorrelation function is discussed.

2. Analytic Properties and Sum Rules

Much of this section parallels that given in I for the density–density response function. First we recall that the self-motion response function $\chi_s(k, z)$ is an analytic function of the complex variable z off the real axis and is given in terms of the spectral function $\chi_s''(k, \omega)$ by(3)

$$\chi_s(k, z) = \int_{-\infty}^{\infty} \frac{d\omega}{\pi} \frac{\chi_s''(k, \omega)}{\omega - z}. \tag{2.1}$$

$\chi_s''(k, \omega)$ is related to Van Hove's incoherent scattering function $S_s(k, \omega)$ defined here as

$$S_s(k, \omega) = \int_{-\infty}^{\infty} dt e^{i\omega(t-t')} \langle e^{-i\mathbf{k}\cdot\mathbf{r}_s(t)} e^{i\mathbf{k}\cdot\mathbf{r}_s(t')} \rangle, \tag{2.2}$$

by the equation

$$S_s(k, \omega) = \frac{2\chi_s''(k, \omega)\hbar}{\rho(1 - e^{-\beta\hbar\omega})}, \tag{2.3}$$

which in the classical limit reads

$$S_s(k, \omega) = \frac{2}{\rho\beta\omega} \chi_s''(k, \omega). \tag{2.4}$$

Even though we shall restrict ourselves to the classical limit, it is for our purposes usually more convenient to deal with the function $\chi_s''(k, \omega)$. The latter is a real, odd function of ω with the property $\omega\chi_s''(k, \omega) \geqslant 0$.

Very useful, exact relations are provided by the moment sum rules for $\chi_s''(k, \omega)$ or $S_s(k, \omega)$. We define the moments

$$\begin{aligned} M_n^{(s)}(k) &= \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega}{\pi}\, \omega^n \chi_s''(k, \omega) = \rho\beta \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega}{\pi}\, \omega^{n+1} S_s(k, \omega) \\ &= \rho\beta \left\langle \left(i \frac{\partial}{\partial t} \right)^{n+1} e^{-i\mathbf{k}\cdot\mathbf{r}_s(t)}\, e^{i\mathbf{k}\cdot\mathbf{r}_s(t')} \right\rangle_{t'=t} . \end{aligned} \tag{2.5}$$

These can in principle be evaluated for all n by making repeated use of the equation of motion. For the two lowest order sum rules one has

$$\begin{aligned} M_{-1}^{(s)}(k) &\equiv \chi_s(k, 0) = \rho\beta, \\ M_1^{(s)}(k) &= \frac{\rho k^2}{m} = \rho\beta k^2 v_T^2, \end{aligned} \tag{2.6}$$

independent of the interaction, where $v_T = (k_B T/m)^{1/2}$ is the mean thermal velocity. For $n \geqslant 1$ it will be useful to introduce the quantities $\langle \omega_s^{2n}(k) \rangle$ by setting

$$M_{2n+1}^{(s)}(k) = \rho\beta k^2 v_T^2 \langle \omega_s^{2n}(k) \rangle. \tag{2.7}$$

The formulae for $\langle \omega_s^2(k) \rangle$ and $\langle \omega_s^4(k) \rangle$ are known explicitly in terms of the interparticle potential $v(r)$ and static correlation functions$^{(8,9)}$:

$$\langle \omega_s^2(k) \rangle = 3k^2 v_T^2 + \Omega_0^2 \equiv 3k^2 v_T^2 + \frac{\rho}{3m} \int \mathrm{d}\mathbf{r}\, g(r) \nabla^2 v(r), \tag{2.8}$$

$$\begin{aligned} \langle \omega_s^4(k) \rangle = {} & 15(kv_T)^4 + 6k^2 v_T^2 \Omega_0^2 + 9 \frac{k^2}{m^2} \left\{ \rho \int \mathrm{d}\mathbf{r}\, g(r) [\hat{\mathbf{k}} \cdot \nabla v(r)]^2 \right. \\ & \left. + \rho^2 \int \mathrm{d}\mathbf{r}_2 \mathrm{d}\mathbf{r}_3\, g_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) [\hat{\mathbf{k}} \cdot \nabla_1 v(r_{12})][\hat{\mathbf{k}} \cdot \nabla_1 v(r_{13})] \right\} \\ & + \frac{1}{m^2} \left\{ 2\rho \int \mathrm{d}\mathbf{r}\, g(r) [\nabla(\hat{\mathbf{k}} \cdot \nabla v(r))]^2 \right. \\ & \left. + \rho^2 \int \mathrm{d}\mathbf{r}_2 \mathrm{d}\mathbf{r}_3\, g_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \nabla_1 [\hat{\mathbf{k}} \cdot \nabla_1 v(r_{12})] \cdot \nabla_1 [\hat{\mathbf{k}} \cdot \nabla_1 v(r_{13})] \right\} \end{aligned} \tag{2.9}$$

where $g(r)$ is the pair distribution function, $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$, $\mathbf{r}_{13} = \mathbf{r}_1 - \mathbf{r}_3$, and $g_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = g_3(0, \mathbf{r}_{12}, \mathbf{r}_{13})$ is the three particle distribution function. Ω_0^2 can be interpreted as a mean square Einstein oscillation frequency of a particle along its trajectory in the fluid.

We shall also make use of the asymptotic expansions for $\chi_s(k, z)$ and $\chi_s^{-1}(k, z)$ for large z. From (2.1) and (2.5) one finds for large z

$$\chi_s(k, z) \sim -\frac{M_1^{(s)}}{z^2}\left[1 + \frac{M_3^{(s)}/M_1^{(s)}}{z^2} + \frac{M_5^{(s)}/M_1^{(s)}}{z^4} + \ldots\right], \tag{2.10}$$

$$\chi_s^{-1}(k, z) \sim -\frac{1}{M_1^{(s)}}\left[z^2 - \frac{M_3^{(s)}}{M_1^{(s)}} + \frac{(M_3^{(s)}/M_1^{(s)})^2 - M_5^{(s)}/M_1^{(s)}}{z^2} + \ldots\right]. \tag{2.11}$$

In the case of free particles, the self-motion response function $\chi_s(k, z)$ is identical with the free particle density–density response function $\chi_0(k, z)$ discussed in detail in I. The large z expansions of $\chi_0(k, z)$ and $\chi_0^{-1}(k, z)$ are obtained from (2.10) and (2.11) by replacing the moments $M_n^{(s)}(k)$ by the corresponding noninteracting values $M_n^{(0)}(k)$ (given by Eqs. (2.6)–(2.9) with $v(r) = 0$).

A quantity which is widely studied in the theory of liquids and which is closely related to the incoherent scattering function is the velocity autocorrelation function $\Phi(t)$ and its associated frequency distribution function $S_v(\omega)$ defined by

$$\Phi(t) = \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} S_v(\omega) e^{-i\omega t}, \tag{2.12}$$

where $\mathbf{v}(t)$ is the velocity of the particle s at time t. From Eq. (2.2) follows the exact relation, valid for a spatially invariant system$^{(10)}$

$$\lim_{k \to 0} \omega^2 S_s(k, \omega) = \frac{k^2}{3} S_v(w). \tag{2.13}$$

From (2.12) we immediately obtain the zeroth moment of $S_v(\omega)$:

$$\int_{-\infty}^{\infty} \frac{d\omega}{2\pi} S_v(\omega) = \langle \mathbf{v}^2(0) \rangle = 3 v_T^2. \tag{2.14}$$

The higher frequency moments of $S_v(\omega)$ are conveniently described by the quantities $\langle \omega_v^{2n} \rangle$ defined by

$$\int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \omega^{2n} S_v(\omega) = 3 v_T^2 \langle \omega_v^{2n} \rangle. \tag{2.15}$$

Using the relation (2.13) we see that the $\langle\omega_v^{2n}\rangle$ are related to the moments of the incoherent scattering function by

$$\lim_{k\to0}\int_{-\infty}^{\infty}\frac{\mathrm{d}\omega}{2\pi}\,\omega^{2n}S_s(k,\omega) = \frac{k^2}{3}\int_{-\infty}^{\infty}\frac{\mathrm{d}\omega}{2\pi}\,\omega^{2n-2}S_v(\omega) = k^2v_T{}^2\langle\omega_v^{2n-2}\rangle. \tag{2.16}$$

Comparing the moment expressions (2.7)–(2.9) with (2.16) we obtain the expressions[5]

$$\langle\omega_v{}^2\rangle = \lim_{k\to0}\langle\omega_s{}^2(k)\rangle = \Omega_0{}^2,$$

$$\begin{aligned}\langle\omega_v{}^4\rangle = \lim_{k\to0}\langle\omega_s{}^4(k)\rangle = \frac{1}{m^2}\biggl\{2\rho\int\mathrm{d}\mathbf{r}g(r)[\nabla(\hat{\mathbf{k}}\cdot\nabla v(r))]^2 \\ +\rho^2\int\mathrm{d}\mathbf{r}_2\mathrm{d}\mathbf{r}_3g_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)\nabla_1(\hat{\mathbf{k}}\cdot\nabla_1v(r_{12}))\cdot\nabla_1(\hat{\mathbf{k}}\cdot\nabla_1v(r_{13}))\biggr\},\end{aligned} \tag{2.17}$$

where $\hat{\mathbf{k}}$ is a unit vector.

To conclude this section let us recall the relation defining the self-diffusion constant D_s:[11]

$$D_s = \frac{1}{3}\int_0^{\infty}\mathrm{d}t\langle\mathbf{v}(t)\cdot\mathbf{v}(0)\rangle \tag{2.18a}$$

$$= \lim_{\omega\to0}\tfrac{1}{6}S_v(\omega). \tag{2.18b}$$

For an ideal gas D_s is infinite, while for a harmonically oscillating atom it is zero. For an atom in a liquid D_s is a finite positive quantity. Using the relations (2.4) and (2.13) we can also express D_s in the forms[4,12]

$$\begin{aligned}D_s &= \lim_{\omega\to0}\left[\lim_{k\to0}\frac{1}{2}\frac{\omega^2}{k^2}S_s(k,\omega)\right] \\ &= \frac{1}{\rho\beta}\lim_{\omega\to0}\left[\lim_{k\to0}\frac{\omega}{k^2}\chi_s''(k,\omega)\right].\end{aligned} \tag{2.18c}$$

(Note that strictly speaking the relations (2.18b) and (2.18c) would predict $D_s = 0$ for an ideal gas, since in this case $S_v(\omega) = 3v_T{}^2\delta(\omega)$, and $\lim_{\omega\to0}\delta(\omega) = 0$, whereas $\delta(0) = \infty$. In order to adhere to the customary definitions of transport coefficients[4] as expressed here by (2.18b) and (2.18c), we shall adhere to the convention that in going to the ideal gas limit, the interaction between particles is to be switched off after the required limits in (2.18b, c) have been taken.)

3. An Exact Representation for $\chi_s(k, z)$ and $\chi_s''(k, \omega)$

In analogy to the discussion given in I for the density–density response function, we propose here an exact representation for $\chi_s(k, z)$ of the form

$$\chi_s(k, z) = \frac{\chi_0(k, z)}{1+\phi_s(k, z)\chi_0(k, z)}, \tag{3.1}$$

or, equivalently

$$\chi_s^{-1}(k, z) = \chi_0^{-1}(k, z)+\phi_s(k, z). \tag{3.2}$$

In I we showed that the above representation amounts to an exact generalization of the mean field approximation, in which the static, effective mean field potential is replaced by one which is also frequency (z) dependent. Accordingly we refer to this representation as the generalized mean field representation, to be distinguished from the generalized hydrodynamic representation considered by some authors(4,12).

The representation (3.1) has the feature that it automatically gives the correct free particle result, $\chi_0(k, z)$, for $\chi_s(k, z)$ when the interaction is switched off. The function $\phi_s(k, z)$ may be considered an effective frequency and wave number dependent interaction acting on the particle s. For the moment we may simply regard (3.2) as the definition of $\phi_s(k, z)$. As shown in I, it is possible to give an equivalent space-time form for the representation (3.1) in terms of an exact ansatz for the equation of motion of the phase–space distribution function describing the particle s. Here we shall use analyticity and sum rule arguments to describe the basic properties which $\phi_s(k, z)$ must satisfy. Below we shall show explicitly the relation between the incoherent scattering function $S_s(k, \omega)$ measured in neutron inelastic experiments and the real and imaginary parts of ϕ_s.

First we observe that because $\chi_s(k, 0)$ and $\chi_0(k, 0)$ are both equal to $\rho\beta$ it follows from (3.2) that $\phi_s(k, 0) = 0$. Second, from the fact that $\chi_s^{-1}(k, z)$ and $\chi_0^{-1}(k, z)$ are analytic functions of z off the real axis,(4) it follows that the same must be true of $\phi_s(k, z)$. Equations (3.2) and (2.11) imply that for large z, $\phi_s(k, z)$ has the asymptotic expansion

$$\phi_s(k, z) = \phi_{s\infty}(k) - \frac{a_s(k)}{z^2} + 0\left(\frac{1}{z^4}\right), \tag{3.3}$$

where

$$\phi_{s\infty}(k) \equiv \phi_s(k, \infty) = \frac{m}{\rho k^2}\Omega_0^2, \tag{3.4}$$

$$a_s(k) = -\frac{m}{\rho k^2}[\langle\omega_s^4(k)\rangle - \langle\omega_s^2(k)\rangle^2 - 6(kv_T)^4]. \tag{3.5}$$

Because $\phi_s(k, z) - \phi_{s\infty}(k)$ is analytic off the real axis and vanishes for large z as $1/z^2$ we may write a spectral representation of the form

$$\phi_s(k, z) - \phi_{s\infty}(k) = \int_{-\infty}^{\infty} \frac{d\omega}{\pi} \frac{\phi_s''(k, \omega)}{\omega - z}, \tag{3.6}$$

where $\phi_s''(k, \omega)$ is a real, odd function of ω given by

$$\phi_s''(k, \omega) = Im\phi_s(k, \omega + i\epsilon). \tag{3.7}$$

By taking $z = 0$ in (3.6) we obtain the sum rule

$$\int_{-\infty}^{\infty} \frac{d\omega}{\pi} \frac{\phi_s''(k, \omega)}{\omega} = -\frac{m\Omega_0^2}{\rho k^2}. \tag{3.8}$$

By comparing (3.3) with the large z expansion of (3.6) we obtain the first moment sum rule for $\phi_s''(k, \omega)$:

$$\int_{-\infty}^{\infty} \frac{d\omega}{\pi} \omega\phi_s''(k, \omega) = a_s(k). \tag{3.9}$$

Higher order moment sum rules for $\phi_s''(k, \omega)$ could be obtained in terms of the moments of $\chi_s''(k, \omega)$. The real part of the effective interaction, to be denoted by $\phi_s'(k, \omega)$ is related to the imaginary part, $\phi_s''(k, \omega)$, by a Kramers–Kronig relation:

$$\phi_s'(k, \omega) - \phi_{s\infty}(k) = P\int_{-\infty}^{\infty} \frac{d\omega'}{\pi} \frac{\phi_s''(k, \omega')}{\omega' - \omega}, \tag{3.10}$$

where P denotes the principal value integral.

From (3.1) the spectral function $\chi_s''(k, \omega)$ is found to be given by

$$\chi_s''(k, \omega) = \frac{\chi_0'' - \phi_s''[(\chi_0')^2 + (\chi_0'')^2]}{[1 + \phi_s'\chi_0' - \phi_s''\chi_0'']^2 + [\phi_s''\chi_0' + \phi_s'\chi_0'']^2} \tag{3.11}$$

and the real part, $\chi_s'(k, \omega)$ of the complex response function $\chi_s(k, \omega + i\epsilon)$ is

$$\begin{aligned}\chi_s'(k, \omega) &= P\int_{-\infty}^{\infty} \frac{d\omega'}{\pi} \frac{\chi_s''(k, \omega')}{\omega' - \omega} \\ &= \frac{\chi_0' + \phi_s'[(\chi_0')^2 + (\chi_0'')^2]}{[1 + \phi_s'\chi_0' - \phi_s''\chi_0'']^2 + [\phi_s''\chi_0' + \phi_s'\chi_0'']^2}.\end{aligned} \tag{3.12}$$

In (3.11) and (3.12) all the arguments of the functions on the right are k, ω. The functions $\chi_0''(k, \omega)$ and $\chi_0'(k, \omega)$ are the corresponding free particle functions discussed in I. Here we quote only the expression for χ_0'':

$$\chi_0''(k, \omega) = \rho\beta \sqrt{\frac{\pi}{2}} \frac{\omega}{kv_T} \exp\left[-\frac{\omega^2}{2k^2v_T^2}\right]. \tag{3.13}$$

The incoherent scattering function $S_s(k, \omega)$ is determined by Eqs. (2.4) and (3.11). Since $\phi_s'(k, \omega)$ is given in terms of $\phi_s''(k, \omega)$ by (3.10), the calculation of $S_s(k, \omega)$ is reduced to the problem of determining $\phi_s''(k, \omega)$. As long as any approximate $\phi_s''(k, \omega)$ satisfies the sum rule (3.8), $S_s(k, \omega)$ will automatically satisfy the zeroth, second and fourth moment sum rules. If in addition, $\phi_s''(k, \omega)$ is chosen to satisfy (3.9), $S_s(k, \omega)$ will also satisfy the sixth moment sum rule, and so on.

It will be useful to note here explicitly the exact expression for $S_s(k, \omega = 0)$, the incoherent scattering function at zero energy transfer. From Eqs. (2.4), (3.11) and (3.13) one finds

$$S_s(k, 0) = \frac{\sqrt{2\pi}}{kv_T} - 2\rho\beta \lim_{\omega \to 0} \frac{\phi_s''(k, \omega)}{\omega}. \tag{3.14}$$

Note that both sides of this equation have the dimension of time. Since $\rho\beta\phi_s''(k, \omega)$ is a dimensionless measure of the effect of interactions, we can rigorously define a quantity $\tau(k)$ having the dimension of time by setting

$$\tau(k)\phi_{s\infty}(k) = -\lim_{\omega \to 0} \frac{\phi_s''(k, \omega)}{\omega}, \tag{3.15}$$

so that (3.14) can be written as

$$S_s(k, 0) = \frac{\sqrt{2\pi}}{kv_T} + 2\rho\beta\phi_{s\infty}(k)\tau(k). \tag{3.16}$$

The relations (3.14) and (3.16) are simple but rigorous consequences of the present formalism and prove very useful in relating or comparing experimental results to theory; they will be applied in the next section. The time $\tau(k)$ is a characteristic " memory " or relaxation time associated with the motion of the selected particle s. It may be interpreted as the average length of time the particle s " remembers " the density fluctuation of wave number k it has undergone at previous times on account of its collisions with the other particles. Even though we are unable to prove it in general, we expect $\tau(k)$ as defined by (3.15) and (3.16) to be positive. In the next section, on the basis of the results obtained by Sköld *et al.*,⁽²⁾ this is in fact found to be the case.

Being an exact representation for the spectral function, Eq. (3.11) must provide (at least in principle) a correct description of phenomena in the entire region of frequencies and wave numbers. In particular, for small values of its arguments, the function $\phi_s''(k, \omega)$ must contain the essential information characterizing the diffusion process which the particle s is undergoing on a long distance-time scale. To see these relations let us first note the expression for the spectrum of the velocity autocorrelation function in terms of $\phi_s'(k, \omega)$ and $\phi_s''(k, \omega)$ From Eqs. (2.4), (2.13) and (3.11) one obtains

$$\begin{aligned} S_v(\omega) &= \lim_{k\to 0} \frac{6\omega}{\rho\beta k^2}\chi_s''(k, \omega) \\ &= \lim_{k\to 0} \frac{-6\rho/mk^2 v_T^2 \omega\phi_s''(k, \omega)}{[\omega^2 - \rho k^2/m\phi_s'(k, \omega)]^2 + [\rho k^2/m\phi_s''(k, \omega)]^2}. \end{aligned} \tag{3.17}$$

In obtaining this result we have made use of the asymptotic expansion for $\chi_0'(k, \omega)$ given by Eq. (3.18) in I. Note from relations (3.3)–(3.10) that the limits as $k \to 0$ of $k^2\phi_s'(k, \omega)$ and $k^2\phi_s''(k, \omega)$ are finite quantities and that $\phi_s'(k, 0) = 0$. It therefore follows that the self-diffusion constant D_s (cf. Eqs. (2.18 a–c)) is given by

$$D_s = \lim_{\omega\to 0} \tfrac{1}{6} S_v(\omega) = \lim_{\omega\to 0}\left[\lim_{k\to 0} -\frac{\omega}{\rho\beta k^2\phi_s''(k, \omega)}\right]. \tag{3.18}$$

Whereas in the defining relations (2.18c) the order in which the limits are taken is important, we might expect that this is not the case for (3.18), i.e. we might expect that $k^2\phi_s''(k, \omega)/\omega$ is well behaved and slowly varying at small k, ω. We can then interchange the limits in (3.18) and using Eqs. (3.15), (3.4) obtain the expression

$$D_s = \frac{k_B T}{m\Omega_0^2\tau(0)}. \tag{3.19}$$

A relation of this form was first derived by Martin and Yip⁽¹³⁾ starting from quite different considerations than the ones presented here. Insofar as the precise meaning of the time $\tau(0)$ is defined by Eq. (3.15), the above relation may simply be looked upon as a useful shorter version of the rigorous expression (3.18). (Noting the analogy between D_s^{-1} and the homogeneous electrical conductivity σ, Martin and Yip⁽¹³⁾ have observed that in the problem of electrical conductivity, (3.19) corresponds to the well-known expression

$$\sigma = \frac{\rho e^2 \tau(0)}{m} = \frac{\omega_p{}^2 \tau(0)}{4\pi m},$$

since $\omega_p{}^2$, the square of the plasma frequency, corresponds closely to $\Omega_0{}^2$.)

It is perhaps also of some interest to note here explicitly the relation between $\phi_s''(k, \omega)$ and the frequency dependent friction " constant " $\gamma'(\omega)$ introduced originally by Martin and Yip.⁽¹³⁾ The latter is the basic quantity in the generalized hydrodynamic description and has been considered more recently by Zwanzig and Bixon⁽¹⁴⁾ on the basis of a generalized Navier-Stokes approach. The link between the formalism presented in this paper and that of the above authors is contained in the relations

$$\lim_{k\to 0} \frac{\rho k^2}{m} \frac{\phi_s''(k, \omega)}{\omega} = -\gamma'(\omega),$$

$$\lim_{k\to 0} \frac{\rho k^2}{m} \frac{\phi_s'(k, \omega)}{\omega} = \gamma''(\omega). \tag{3.20}$$

Thus the generalized frequency-dependent friction constant analysis of single-particle motion presented by the above authors⁽¹³,¹⁴⁾ can be considered and obtained as a limiting case ($k \to 0$) of the present generalized mean field formalism.

To conclude this section we remark that similar arguments to those given in Sec. 3 of I can be made concerning a possible experimental determination of the function $\phi_s''(k, \omega)$ from the measured incoherent scattering function in a certain region of k and ω values.

4. Ansatz forms for ϕ_s'' and the calculation of $S_s(k, \omega)$

The determination of $\phi_s''(k, \omega)$ would be the task of detailed microscopic calculations. Thus far, however, the complexity of the problem has not allowed any simple, reliable results to be obtained. Much can therefore be learned by making assumptions about the behaviour of $\phi_s''(k, \omega)$ and testing these assumptions by comparing the results obtained with experimental data. In this section we therefore consider two simple forms for the function $\phi_s''(k, \omega)$ and evaluate the corresponding incoherent scattering function $S_s(k, \omega)$.

The forms we consider are a Lorentzian type form

$$\phi_s''(k, \omega) = -\frac{\phi_{s\infty}(k)\omega\tau_1(k)}{1+\omega^2\tau_1^2(k)}, \tag{4.1}$$

with corresponding real part given by

$$\phi_s'(k, \omega) = \frac{\phi_{s\infty}(k)\omega^2\tau_1^2(k)}{1+\omega^2\tau_1^2(k)}, \tag{4.2}$$

and a Gaussian type form

$$\phi_s''(k, \omega) = -\phi_{s\infty}(k)\omega\tau_2(k)\exp\left[-\frac{\omega^2\tau_2^2(k)}{\pi}\right], \tag{4.3}$$

with corresponding real part

$$\phi_s'(k, \omega) = \phi_{s\infty}(k)2u\mathrm{F}(u), \tag{4.4}$$

where $u = \omega\tau_2(k)/\sqrt{\pi}$ and $\mathrm{F}(u)$ is Dawson's integral, already encountered in I. Both the above forms (4.1) and (4.3) satisfy the basic sum rule (3.8) and both are in accord with the relation (3.15) defining the relaxation time $\tau(k)$. The reason we have chosen to put on subscripts on $\tau(k)$ in (4.1) and (4.3) will become clear in what follows.

First it must, however, be pointed out that the form (4.1) does not have a finite first frequency moment as required by the sum rule (3.9). Moreover, the complex potential corresponding to (4.1),

$$\phi_s(k, z) = \frac{\phi_{s\infty}(k)iz\tau_1(k)}{iz\tau_1(k) \mp 1}, \tag{4.5}$$

(where the upper (lower) sign corresponds to z in the upper (lower) half complex plane, respectively) is not consistent with the form of the asymptotic expansion (3.3). Nevertheless, (4.1) and (4.2) turn out to give a very good description of the observed incoherent scattering function.

The expression for $S_s(k, \omega)$ is obtained by substituting (4.1), (4.2) or (4.3), (4.4) into Eqs. (2.4) and (3.11). The resulting expressions satisfy the zeroth, second and fourth moment sum rules for $S_s(k, \omega)$, regardless of how the relaxation times $\tau_1(k)$ and $\tau_2(k)$ are determined.

In the case of the Lorentzian form (4.1), we cannot employ any sum rule arguments to determine $\tau_1(k)$ in terms of microscopic quantities so that recourse will be made to experimental data (see below). On the other hand, for the Gaussian form (4.3) we can determine $\tau_2(k)$ by requiring that the first moment sum rule (3.9) for $\phi_s''(k, \omega)$ be also satisfied. When this is done we obtain $\tau_2(k)$ as

$$\tau_2{}^2(k) = -\frac{\pi\phi_{s\infty}(k)}{2a_s(k)} = \frac{\pi/2\Omega_0{}^2}{\langle\omega_s{}^4(k)\rangle - \langle\omega_s{}^2(k)\rangle^2 - 6(kv_T)^4}. \quad (4.6)$$

With this choice for $\tau_2(k)$ the corresponding $S_s(k, \omega)$ satisfies all moment sum rules up to and including the sixth.

Unfortunately, the quantity $\langle\omega_s{}^4(k)\rangle$ defined by Eq. (2.9) has not been calculated; only the limiting value as $k \to 0$ has been estimated (see below). In the absence of knowledge of $\langle\omega_s{}^4(k)\rangle$ we therefore proceed to evaluate both $\tau_2(k)$ and $\tau_1(k)$ from experimental data. The most convenient way of doing this is to make use of the exact relation (3.14) which, using the forms (4.1) and (4.3) yields $\tau_1(k) = \tau_2(k) \equiv \tau(k)$ with $\tau(k)$ related to $S_s(k, 0)$ by (3.16):

$$\tau(k)\left(\frac{2\Omega_0{}^2}{k^2 v_T{}^2}\right) = S_s(k, 0) - \frac{\sqrt{2\pi}}{kv_T}. \quad (4.7)$$

We use the experimental values of $S_s(k, 0)$ obtained by Sköld *et al.*⁽²⁾ from neutron scattering on liquid argon 36 and a mixture of argon 36 and argon 40 at a temperature of 85.2 °K. For $\Omega_0{}^2$ we have used the value $\Omega_0{}^2 = 45 \times 10^{24}\,\text{sec}^{-2}$ calculated by Nijboer and Rahman⁽⁵⁾ for liquid argon at $T = 85.5$ °K and mass density $\rho m = 1.407\ \text{gcm}^{-3}$. (A table of values of $\Omega_0{}^2$ as a function of ρ and T has been given by Levesque and Verlet⁽⁶⁾.)

Table 1 Values for the quantities $\tau(k)$ and $\langle\omega_s{}^4(k)\rangle$ as determined from Eqs. (4.7) and (4.6), respectively, using experimental data for $S_s(k, \omega = 0)$ obtained by Sköld *et al.*⁽²⁾

$k(\text{Å}^{-1})$	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6
$\tau(k)$ (10^{-13} sec)	1.66	1.50	1.30	1.21	1.19	1.18	1.13	1.05	0.91
$\langle\omega_s{}^4(k)\rangle$ ($10^{50}\,\text{sec}^{-4}$)	50.7	60.0	72.2	81.8	88.2	94.2	105	122	152

$k(\text{Å}^{-1})$	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4
$\tau(k)$ (10^{-13} sec)	0.75	0.65	0.62	0.59	0.55	0.51	0.44	0.38	0.35
$\langle\omega_s{}^4(k)\rangle$ ($10^{-50}\,\text{sec}^{4}$)	203	255	289	321	372	433	551	707	829

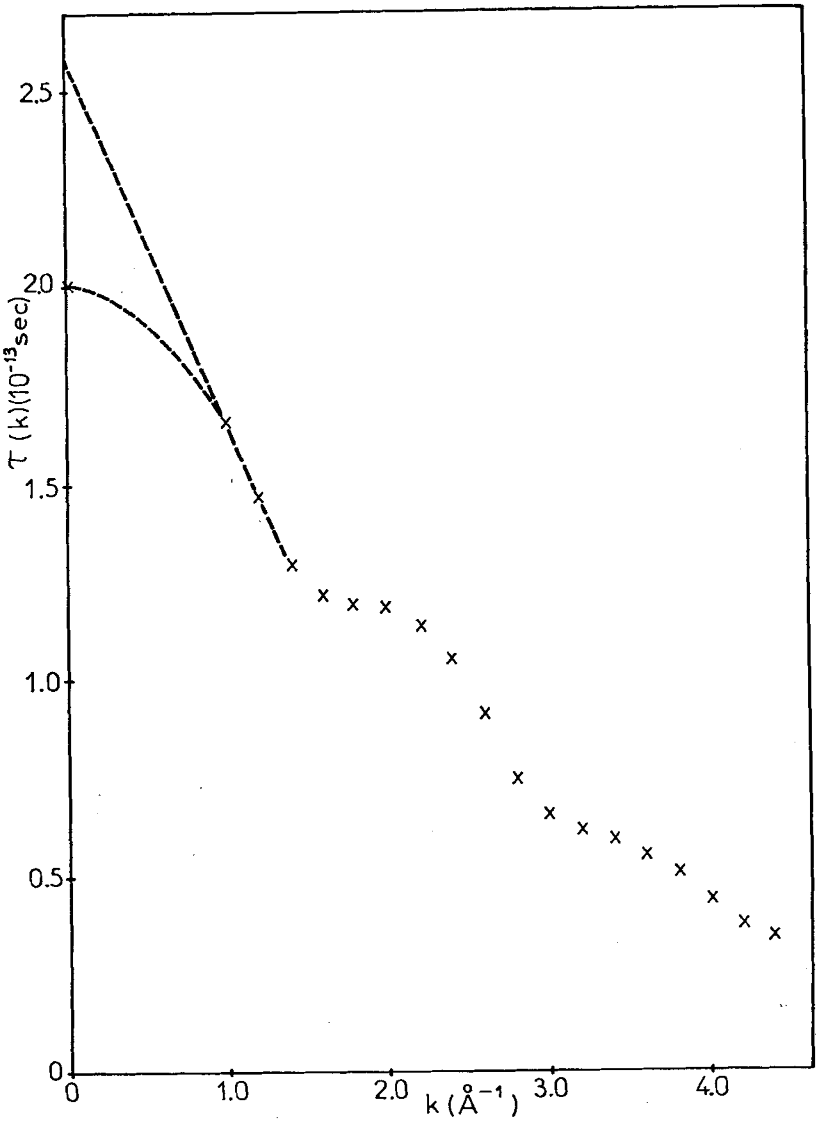


Figure 1. Wave number dependence of the " memory ", or relaxation time $\tau(k)$ for single particle motion, as obtained from Eq. (4.7). The dashed lines represent, respectively, a linear extrapolation to $k=0$, and a smooth join up to the value $\tau(0)=2.04\times10^{-13}$ sec obtained from the experimental diffusion constant via Eq. (3.19).

The resulting values for $\tau(k)$ are given in Table 1 and plotted in Fig. 1. We see that there is hardly any structure, except perhaps near $k = 2.0$ Å^{-1}, and $\tau(k)$ is a continuously decreasing function in the region $1 < k < 4.4$ Å^{-1}. These findings are in agreement with some results of Desai's calculations.(7)

Going back to Eq. (4.6) we can now use the experimentally determined $\tau_2(k)$ together with the knowledge of $\langle\omega_s^2(k)\rangle$ to obtain the hitherto unknown quantity $\langle\omega_s^4(k)\rangle$. These values are also given in Table 1.

In connection with the experimental results of Sköld *et al.*,(2) it should be pointed out that these authors have compared their data for $S_s(k, 0)$ with the result expected from the diffusion law(11) ($S_s(k, 0) = 2/D_sk^2$), finding an agreement to within 10 % over the region $1.0 < k < 4.4$ Å^{-1} with a value $D_s = 1.94 \times 10^{-5}$ cm^2/sec obtained from Naghizadeh and Rice.(15) This wide range of applicability of the hydrodynamic diffusion law is perhaps surprising and indicates that the free particle limit ($S_s(k, 0) = \sqrt{2\pi}/kv_T$) is reached only for k values significantly larger than 4.4 Å^{-1}. From their results Sköld *et al.* conclude that the motion of the atoms in liquid argon are dominated by the diffusive motion and that the vibrational motions are heavily damped.

With the values $\tau_1(k) = \tau_2(k) = \tau(k)$ given in Table 1, one can now easily calculate the incoherent scattering function $S_s(k, \omega)$ for all ω by substituting the Lorentzian forms (4.1), (4.2) or Gaussian forms (4.3), (4.4) into the basic formulae (3.11) and (2.4). The results are shown by the solid (for the Lorentzian) and dashed lines (for the Gaussian) in Figs. 2 and 3 for several values of k. In spite of our fitting to the experimental values at $\omega = 0$, the general agreement between the calculated curves and the experimental points can be considered excellent. Note that Fig. 2 is a plot on a logarithmic scale and that as a result discrepancies for large ω where the scattered intensity is small are magnified.

The ansatz functions (4.1)–(4.4) also determine the form of the spectrum for the velocity autocorrelation function. Substituting (4.1) and (4.2) into (3.17) we find for the Lorentzian ansatz

$$S_v(\omega) = \frac{6v_T^2\Omega_0^2\tau_1(0)[1+\omega^2\tau_1^2(0)]}{\omega^2[1+\tau_1^2(0)(\omega^2-\Omega_0^2)]^2+\Omega_0^4\tau_1^2(0)}, \tag{4.8}$$

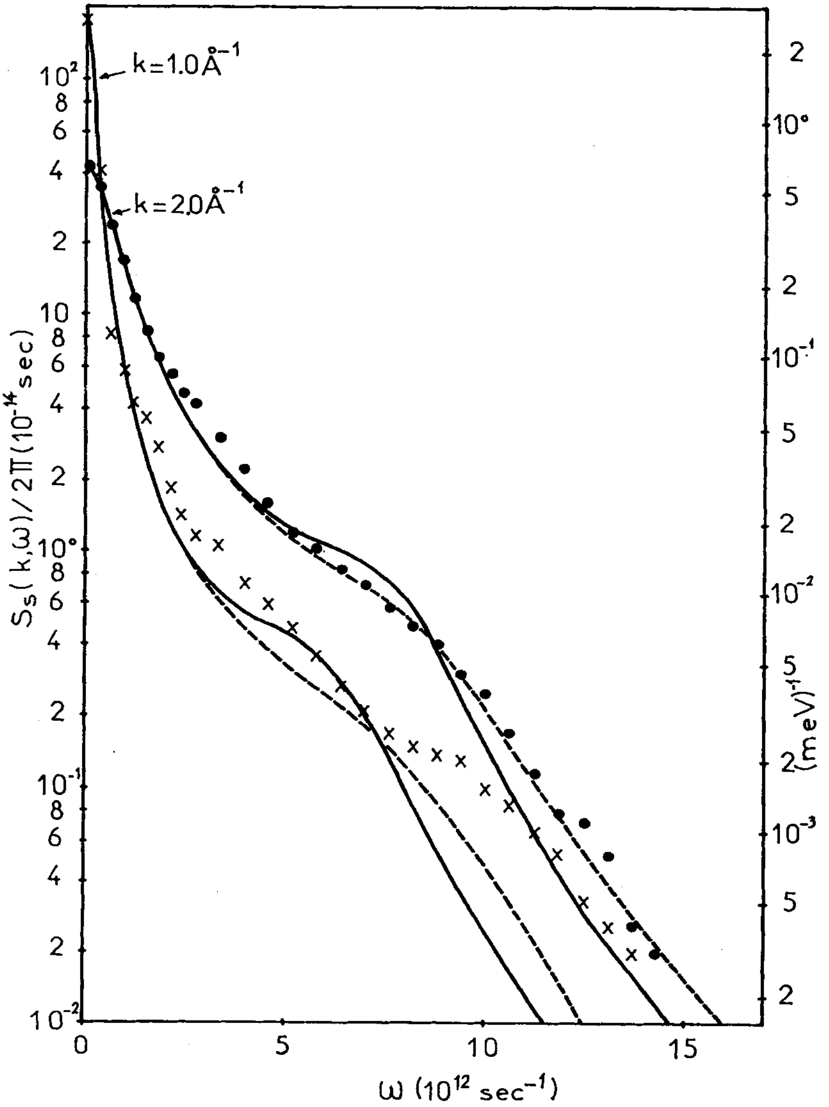


Figure 2. Plot on a logarithmic scale of the incoherent scattering function $S_s(k, \omega)/2\pi$ as a function of ω for $k = 1.0$ and 2.0 Å^{-1}. The solid and dashed lines represent the results of the theory outlined in Sec. 4.

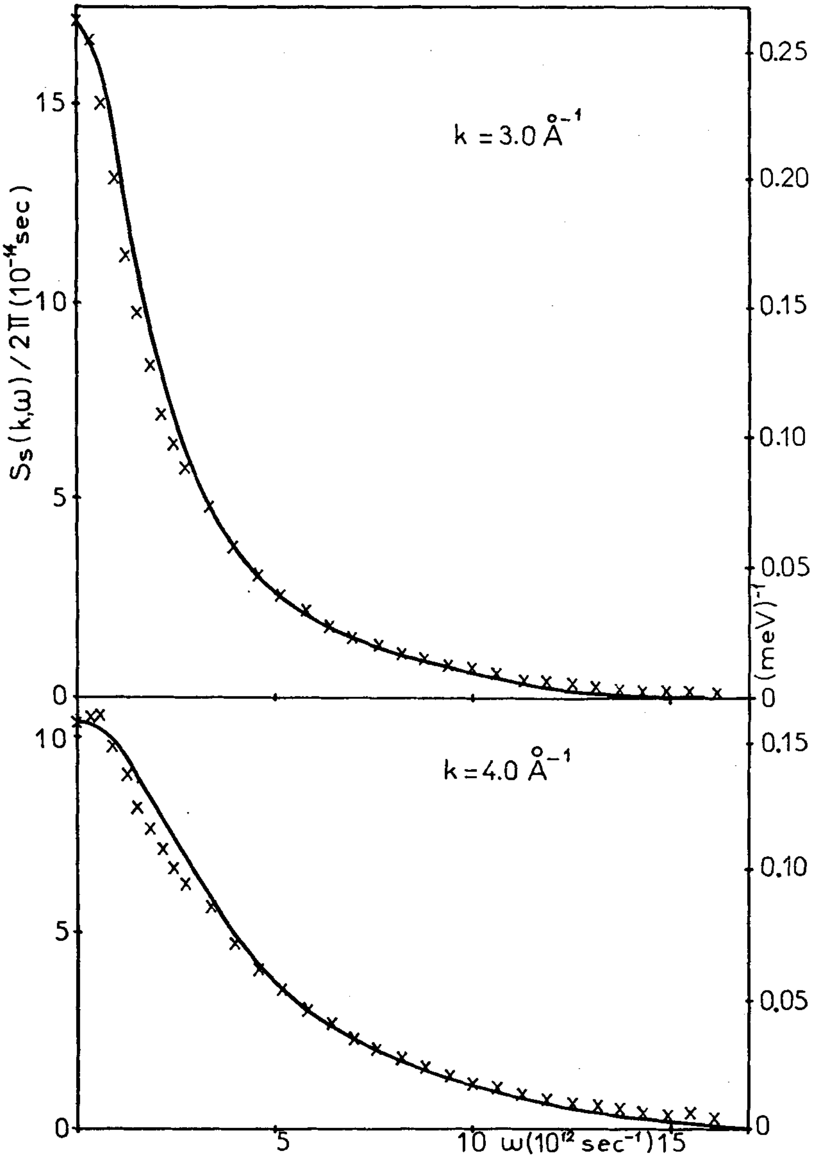


Figure 3. Plot of the incoherent scattering function $S_s(k, \omega)/2\pi$ for $k = 3.0$ and 4.0 Å^{-1}. The crosses denote the experimental results of Sköld *et al.* (Ref. 2). For these k values the results of the Gaussian approximation (Eqs. (4.3), (4.4)) is indistinguishable from those of the Lorentzian approximation (Eqs. (4.1), (4.2)).

while (4.3), (4.4) give for the Gaussian ansatz

$$S_v(\omega) = \frac{6v_T{}^2\Omega_0{}^2\tau_2(0)\exp[-\omega^2\tau_2{}^2(0)/\pi]}{[\omega-(2\Omega_0{}^2/\sqrt{\pi})\tau_2(0)\mathrm{F}(\omega\tau_2(0)/\sqrt{\pi})]^2+\Omega_0{}^4\tau_2{}^2(0)\exp[-2\omega^2\tau_2{}^2(0)/\pi]}. \tag{4.9}$$

The self-diffusion constant D_s corresponding to the above expressions is given by the formula (3.19) with $\tau_1(0)$, $\tau_2(0)$ in place of $\tau(0)$. The above expressions (4.8) and (4.9) have been considered by Martin and Yip⁽¹³⁾ and can be found plotted in Fig. 1 of their paper. In order to be able to calculate $S_v(\omega)$, or to obtain the value of D_s from the formula (3.19), one needs to know the value $\tau_1(0)$ or $\tau_2(0)$.

Unfortunately, the " experimental " values of $\tau(k)$ given in Table 1 extend down only to $k = 1.0$ Å^{-1} so that it is not possible to give a reliable value for $\tau(0)$. A linear extrapolation to $k = 0$ of the values plotted in Fig. 1 would yield the value $\tau(0) = 2.6 \times 10^{-13}$ sec. If we used the " theoretical " value of $\tau_2(k)$ as determined by (4.6) we obtain

$$\tau_2{}^2(0) = \frac{(\pi/2)\Omega_0{}^2}{\langle\omega_v{}^4\rangle - \Omega_0{}^4}, \tag{4.10}$$

(where we have used the relations (2.17)), which when substituted into (3.19) and (4.9) provides a way of calculating⁽¹³⁾ D_s and $S_v(\omega)$ in terms of the equilibrium quantities $\langle\omega_v{}^4\rangle$ and $\Omega_0{}^2$. Using the value $\langle\omega_v{}^4\rangle \simeq 66.5 \times 10^{50}$ sec^{-4} estimated by Nijboer and Rahman,⁽⁵⁾ one finds $\tau_2(0) \simeq 1.24 \times 10^{-13}$ sec and $D_s = 3.16 \times 10^{-5}$ cm^2/sec, in poor agreement with the experimental value quoted above.

If we " invert " the problem and use the experimental value⁽²⁾ $D_s = 1.94 \times 10^{-5}$ cm^2/sec to compute $\tau(0)$ from (3.19), we find $\tau(0) = 2.04 \times 10^{-13}$ sec, which ties in well with the values plotted in Fig. 1. Note that a value $\tau_2(0) = 2.04 \times 10^{-13}$ sec, together with the relation (4.10) would then imply $\langle\omega_v{}^4\rangle = 37.3 \times 10^{50}$ sec^{-4}, instead of the above quoted value found by Nijboer and Rahman.⁽⁵⁾

Acknowledgements

I should like to thank W. F. Saam for a reading of the manuscript and useful comments regarding the content, and R. Lechner for his interest in this work.

REFERENCES

1. Kugler, A. A., submitted to *Ann. Phys.* (*N.Y.*).
2. Sköld, K., Rowe, J. M., Ostrowski, G. and Randolph, P. D., *Phys. Rev.* (to be published).
3. Kadanoff, L. P. and Martin, P. C., *Ann. Phys.* (*N.Y.*) **24**, 419 (1963).
4. Martin, P. C., in *1967 Les Houches Lectures*, Gordon and Breach, New York, 1968, Chs. A–C.
5. Nijboer, B. R. A. and Rahman, A., *Physica* **32**, 415 (1966).
6. Levesque, D. and Verlet, L., *Phys. Rev.* **A2**, 2514 (1970).
7. Desai, R. C., *Phys. Rev.* **A3**, 320 (1971).
8. de Gennes, P. G., *Physica* **25**, 825 (1959).
9. Kim, K. and Nelkin, M., *Phys. Rev.* **A4**, 2065 (1971).
10. Egelstaff, P. A., in *1961 Inelastic Scattering of Neutrons in Solids and Liquids*, I.A.E.A., Vienna, p. 25.
11. Egelstaff, P. A., *An Introduction to the Liquid State*, Academic Press, New York, 1967, p. 134.
12. Chung, C. H. and Yip, S., *Phys. Rev.* **182**, 323 (1969).
13. Martin, P. C. and Yip, S., *Phys. Rev.* **170**, 151 (1968).
14. Zwanzig, R. and Bixon, M., *Phys. Rev.* **A2**, 2005 (1970).
15. Naghizadeh, J. and Rice, S. A., *J. Chem. Phys.* **36**, 2710 (1963).