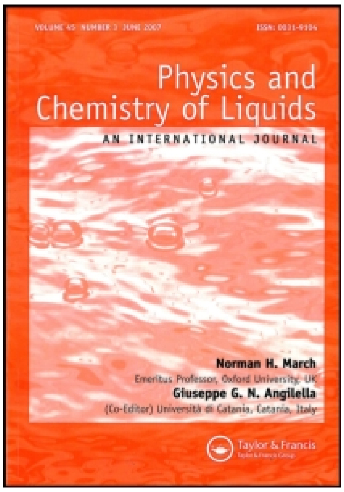

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Relations Between Atomic Transport Coefficients in Simple Liquids and Moments of Neutron Scattering Functions

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Abstract—A possible alternative to Kubo theory is discussed for relating atomic transport coefficients in simple liquids. The arguments used result in a new expansion, in which the density–density response function χ is expanded in a power series in the self response function χ_s. The coefficients of this expansion can be determined, in principle, to all orders, from the moments of the neutron scattering functions $S(q\omega)$ and $S_s(q\omega)$. It is then proposed, by appeal to the hydrodynamic equations, that the radius of convergence of this series can be used to relate diffusion to the sound wave attenuation coefficient. Finally, this χ–χ_s expansion allows a direct comparison of the exact theory presented in this paper with earlier approximate theories relating incoherent and coherent neutron scattering from liquids.

1. Introduction

So far, two principal approaches to the problem of calculating atomic transport coefficients in simple liquids are available. The first of these, historically, considers the full non-equilibrium problem, and is based on the calculation of the perturbed distribution function. Important progress has been made with this method, which is extensively reviewed by Rice and Gray.[1] The second approach, the correlation function formalism of Green,[2] and now often associated with the Kubo[3] treatment of transport coefficients, does not get involved at all in the calculation of non-equilibrium distribution functions, but the transport process is linked to the decay of fluctuations in an equilibrium ensemble. In practice, what one needs in this second method is a detailed knowledge of the appropriate frequency and wave vector dependent response functions in the small q, small ω, limit (Eqs. (1.5) and (1.6) below).

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The purpose of this paper is to discuss a third method, which we believe to have some practical advantages over either of the two methods discussed above, although, in its philosophy, it remains close to the Green–Kubo formalism. This connection will immediately be clear in that we shall make extensive use of response function theory, linking this later, at least in an approximate way, with the hydrodynamic regime. One aim will be to express the atomic transport coefficients in terms of the static correlation functions of the dense liquid.

The density–density response function $\chi(q\omega)$ may be defined as follows. If we switch on an interaction Hamiltonian of the form

$$H_{\text{int}}(t) = -\int d\mathbf{r}\ V_{\text{ext}}(\mathbf{r}t)\,\rho(\mathbf{r}) \tag{1.1}$$

where

$$\rho(\mathbf{r}) = \sum_i \delta(\mathbf{r}-\mathbf{r}_i) \tag{1.2}$$

then the corresponding density change $\delta\rho$ induced by $V_{\text{ext}}(\mathbf{r}t)$ may be written, in terms of the double Fourier transform $V_{\text{ext}}(q\omega)$ with respect to $\mathbf{r}$ and t

$$\delta\rho(q\omega) = \chi(q\omega)\ V_{\text{ext}}(q\omega). \tag{1.3}$$

$\chi(q\omega)$ in Eq. (1.3) is the density–density response function, the calculation of which is the prime task in this paper.

If the external potential is coupled only to a selected particle at $\mathbf{r}_s$, through the corresponding density $\rho^s(\mathbf{r}t) = \delta(\mathbf{r}-\mathbf{r}_s(t))$ then the change in ρ^s may be written as

$$\delta\rho^s(q\omega) = \chi_s(q\omega)\ V_s(q\omega) \tag{1.4}$$

where $\chi_s(q\omega)$ is a response function often referred to as the self part of $\chi(q\omega)$.

As is well known, these two response functions determine the diffusion coefficient D and the sound wave attenuation coefficient $\Gamma = \frac{4}{3}\eta + \zeta$, where η and ζ are the shear and bulk viscosities respectively, through the Kubo relations

$$D = \lim_{\omega\to 0}\ \lim_{q\to 0} \frac{\omega\chi_s''(q\omega)}{q^2} \tag{1.5}$$

and

$$\Gamma = \lim_{\omega\to 0}\ \lim_{q\to 0} \frac{M^2\omega^3\chi''(q\omega)}{q^4} \tag{1.6}$$

where χ_s'' and χ'' are the imaginary parts of χ_s and χ respectively.

The eventual object therefore of the present approach is to replace these equations by relations that involve only static equilibrium properties. There is a solution to this problem, at least in principle, since both $\chi(q\omega)$ and $\chi_s(q\omega)$ possess a high frequency expansion, with expansion coefficients that are expressed solely in terms of the static correlation functions and the pair potential. If these series could be summed up, then, by substituting the results into Eqs. (1.5) and (1.6), the desired expressions for diffusion and viscosity would result. However, because of the extreme complexity of this series, there is, at present, little hope of achieving this summation.

The approach we adopt here is based on the observation that, although the moment expansions of χ and χ_s cannot be summed up, useful information can be written down for their radius of convergence. It is then argued that these radii of convergence determine the modulus of the complex frequencies, though not the phase, where $\chi(q\omega)$ and $\chi_s(q\omega)$ have poles arising from collisions. In Sec. 2, we therefore derive expressions for these radii of convergence in terms of the moments. We show there, however, that though the sound wave attenuation coefficient is related to the phase of a pole, it is not determined by the radius of convergence of the moment expansion for χ. In Sec. 4 we therefore convert the moment expansion, which is an expansion in powers of $(1/i\omega)^2$ into a power series in χ_s. In Sec. 5, we suggest that the radius of convergence of this new series may relate D to Γ. We conclude by discussing in Sec. 6 various approximations suggested earlier in the light of this new expansion, and the relation to neutron scattering in Sec. 7.

2. Radius of Convergence of Moment Expansion

In the classical limit, the fluctuation–dissipation theorem allows us to write the Laplace transform of $\chi(qt)$ and $\chi_s(qt)$ as

$$\chi(qp) = -\beta \int_0^\infty dt\, e^{-pt} \frac{\partial F(qt)}{\partial t} \tag{2.1}$$

and

$$\chi_s(qp) = -\beta \int_0^\infty dt\, e^{-pt} \frac{\partial F_s(qt)}{\partial t} \tag{2.2}$$

where $F(qt)$ and $F_s(qt)$ are the density–density correlation function and its self part respectively, defined by

$$F(qt) = \langle \rho_q(t)\, \rho_{-q}(0) \rangle \tag{2.3}$$

and

$$F_s(qt) = \langle \rho_q{}^s(t)\, \rho^s{}_{-q}(0) \rangle \tag{2.4}$$

where $\rho_q = \sum_i e^{i\mathbf{q}\cdot\mathbf{R}_i}$ and $\rho_q{}^s = e^{i\mathbf{q}\cdot\mathbf{R}_s}$, $\mathbf{R}_i$ denoting the position vector of the ith particle.

By successive partial integrations, both Eqs. (2.1) and (2.2) can be turned into power series in $(1/p^2)$, and we may write

$$\chi(qp) = \sum_{n=1}^{\infty} \alpha_n \left(\frac{1}{p^2}\right)^n \tag{2.5}$$

and

$$\chi_s(qp) = \sum_{n=1}^{\infty} \gamma_n \left(\frac{1}{p^2}\right)^n \tag{2.6}$$

where

$$\alpha_n = \beta \frac{\partial^{2n}}{\partial t^{2n}} F(qt)\bigg|_{t=0} = \beta(-1)^n \langle \rho_q{}^{(n)}(0)\, \rho^{(n)}_{-q}(0) \rangle \tag{2.7}$$

$$\gamma_n = \beta \frac{\partial^{2n}}{\partial t^{2n}} F_s(qt)\bigg|_{t=0} = \beta(-1)^n \langle \rho_q{}^{s(n)}(0)\, \rho^{s(n)}_{-q}(0) \rangle. \tag{2.8}$$

Here, use has been made of the fact that odd derivatives of both $F(qt)$ and $F_s(qt)$ vanish at $t = 0$, on account of time reversal invariance. Equations (2.5) and (2.6) are often referred to as the moment expansions of the response functions χ and χ_s, for the coefficients α_n and γ_n may also be written as

$$\alpha_n = \beta(-1)^n \int \frac{d\omega}{2\pi}\, \omega^{2n} S(q\omega) \equiv \beta(-1)^n \langle \omega^{2n} \rangle \tag{2.9}$$

and

$$\gamma_n = \beta(-1)^n \int \frac{d\omega}{2\pi}\, \omega^{2n} S_s(q\omega) \equiv \beta(-1)^n \langle \omega^{2n} \rangle_s \tag{2.10}$$

where $S(q\omega)$ and $S_s(q\omega)$ are the coherent and incoherent scattering functions respectively, related to $F(qt)$ and $F_s(qt)$ by Fourier transformation.

It is clear from Eqs. (2.7) and (2.8) that the expansion coefficients α_n and γ_n are completely determined by the static correlation functions and the pair potential, provided the total potential energy is assumed to consist solely of two-particle terms. Therefore, the objective of the present work would be achieved if we could write the transport coefficients Γ and D in terms of the α_n's and γ_n's. It is also evident that the reason why this cannot be done by simply substituting Eqs. (2.5) and (2.6) into the appropriate Kubo relations is that they diverge for small p. In fact, their radii of convergence are given by

$$\lim_{n\to\infty}\left|\frac{\alpha_{n+1}}{\alpha_n}\right| = r^2 \tag{2.11}$$

and

$$\lim_{n\to\infty}\left|\frac{\gamma_{n+1}}{\gamma_n}\right| = (r^s)^2, \tag{2.12}$$

provided there are no spurious poles. If there are, methods exist for getting round the difficulty, but we shall not go into this here. Thus, in the case where the limits in Eqs. (2.11) and (2.12) exist, the smallest value of p for which we can still use the moment expansion is $p > r$ and $p > r^s$.

The first point which now emerges from our considerations is that the information provided by the coefficients α_n and γ_n as to the radius of convergence of the series for χ and χ_s, when combined with the knowledge of the analytic properties of the response functions χ and χ_s in the complex p-plane is sufficient to define collision times, which it may be possible to relate to Γ and D.

3. Hydrodynamic Regime and Analytic Properties of Response Functions

To obtain further knowledge of the analytic properties of χ and χ_s which we need, we must now turn to the hydrodynamic equations. Naturally, these equations are only valid in the long wavelength and long time regime, and we must therefore be careful to keep in mind this restriction.

Let us consider the function $\chi(qz)$ as the analytic continuation of $\chi(qp)$ away from the real p-axis into the whole complex plane. We shall also assume that we are dealing with a simple viscous fluid without thermal diffusion ($c_p/c_v = 1$) though this restriction is not

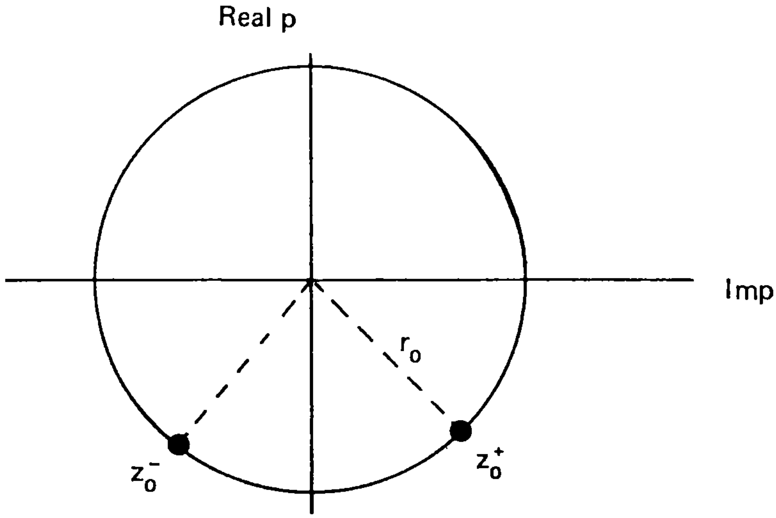

Figure 1.

difficult to remove. Under such circumstances, it is well known from the work of many authors that the requirement that, for small spatial variations and for long times, a density fluctuation must satisfy the macroscopic equations of hydrodynamics implies that $\chi(qz)$ must have two simple poles in the lower half of the complex plane, given by the expression

$$\chi(qz) = \frac{q^2}{M}\frac{1}{z^2+2\Gamma q^2 z+\omega_q{}^2} \tag{3.1}$$

where $\omega_q{}^2 = v_s{}^2 q^2$, with v_s the velocity of sound.

Furthermore, causality and thermodynamic stability require that $\chi(qz)$ be analytic everywhere in the upper half of the complex plane. It then follows from the theory of analytic functions that a $(1/z^2)$ expansion will converge along the real axis, up to, but not including, the point where the circle about the origin, $(1/p^2) = 0$, which goes through the nearest pole, intersects the real axis. Hence by inspection of Fig. 1, we conclude that, with the notation shown there,

$$r_0{}^2 = z_0{}^+ z_0{}^- = \omega_q{}^2 = v_s{}^2 q^2 \tag{3.2}$$

where $z_0{}^+$ and $z_0{}^-$ are the positions of the poles. From Eq. (3.1), these are given by

$$z_0{}^{\pm} = -\Gamma q^2 \pm i\sqrt{\omega_q{}^2-(\Gamma q^2)^2}. \tag{3.3}$$

It should be noted that, as $q \to 0$, $r_0 \to 0$. But, from (2.11), the moment expansion converges to finite r as $q \to 0$. Thus r and r_0 in general cannot be identified. If we had assumed that the coefficients α_n can be used to evaluate r_0^2 then the sound velocity v_s would have been

$$\lim_{q\to 0} \frac{1}{q^2} \lim_{n\to\infty} \left|\frac{\alpha_{n+1}}{\alpha_n}\right|. \tag{3.4}$$

Though the exact evaluation of the coefficients α_n and α_{n+1} for large n shows that the $q \to 0$ limit diverges, it is of some interest that if we estimate the limit in Eq. (3.4) from the low order ratios, and form therefore α_2/α_1 we obtain

$$\frac{1}{q^2} \left.\frac{\alpha_2}{\alpha_1}\right| = \frac{3}{\beta m} + \frac{\rho}{mq^2} \int \mathrm{d}\mathbf{r}\, g(r)\, [1 - \cos qz] \frac{\partial^2 \phi}{\partial z^2} \tag{3.5}$$

where $\phi(r)$ is the pair potential. Except for the kinetic term $3/\beta m$, which is very small for a dense fluid, this is the same result as that obtained recently by Hubbard and Beeby,[4] for the velocity of sound.

Also by making the " decoupling " on the moments, such that

$$\frac{\alpha_{n+1}}{\alpha_n} = \frac{\langle \omega^{2n+2} \rangle}{\langle \omega^{2n} \rangle} = \frac{\langle \omega^{2n} \rangle \langle \omega^2 \rangle}{\langle \omega^{2n} \rangle \langle 1 \rangle} = \frac{\langle \omega^2 \rangle}{\langle 1 \rangle}, \tag{3.6}$$

we obtain the usual " independent phonon " result, namely that

$$\omega_q^2 = \frac{q^2}{\beta m S(q)}. \tag{3.7}$$

Unfortunately, the radius of convergence r is not sufficient to determine the sound velocity v_s in any rigorous way. If one could get r_0, one must also know the phase of the complex numbers $z_0^\pm$ determining the position of the pole, in order to calculate Γ. Such information is not, unfortunately, available from the coefficients α_n; as

$$\lim_{n\to\infty} \left|\frac{\alpha_{n+1}}{\alpha_n}\right|$$

is related to a collision time.

There is a possible way round this difficulty, however, as we shall now discuss. If we convert the moment expansion for χ into a power series in terms of another variable, and, as it happens, one very convenient choice of this variable is χ_s, then by an analysis entirely similar to the foregoing discussion, one can attempt to relate Γ and the diffusion constant D.

To conclude this section, we turn to the moment expansion for the self part of the response function χ_s. Since χ_s describes the meanderings of a randomly selected atom in a dense liquid environment, it is clear that in the hydrodynamic limit it must describe self diffusion. This leads to the conclusion that, for small q, a pole of χ_s is described by

$$\chi_s(qp) = \frac{\beta D q^2}{p + Dq^2} \tag{3.8}$$

that is to say, χ_s has a simple pole at $p = -Dq^2$. Consequently, from Fig. 2, it is tempting to identify the radius of convergence of the moment expansion given by Eq. (2.6), namely

$$(r^s)^2 = \lim_{n \to \infty} \left| \frac{\gamma_{n+1}}{\gamma_n} \right| \tag{3.9}$$

with the square of the diffusion coefficient times q^2. D would then be obtained from

$$\lim_{q \to 0} \frac{1}{q^4} \lim_{n \to \infty} \left| \frac{\gamma_{n+1}}{\gamma_n} \right|. \tag{3.10}$$

Unfortunately, it is not possible to make even a rough first estimate of D from the first few moments, for these give the wrong q dependence. Thus we have

$$\frac{\gamma_2}{\gamma_1} = \frac{3q^2}{\beta m} + \frac{\rho}{m} \int \mathrm{d}\mathbf{r}\, g(r) \frac{\partial^2 \phi}{\partial z^2}. \tag{3.11}$$

The origin of this difficulty is that we must expect that if we can follow the ratio of successive moments to higher and higher order, this must eventually give a constant for the ratio γ_{n+1}/γ_n, which again we can take to constitute a definition of a collision time. It may again prove possible to relate this to D.

4. Expansion of χ in terms of χ_s

We have seen that no simple way of getting Γ and D out of the moment expansions is afforded by the above discussion. We turn therefore to an alternative expansion in this section, in which we shall convert the moment expansion for the response function $\chi(q, p)$ into a power series in $\chi_s(q, p)$. It will be seen later that, as a

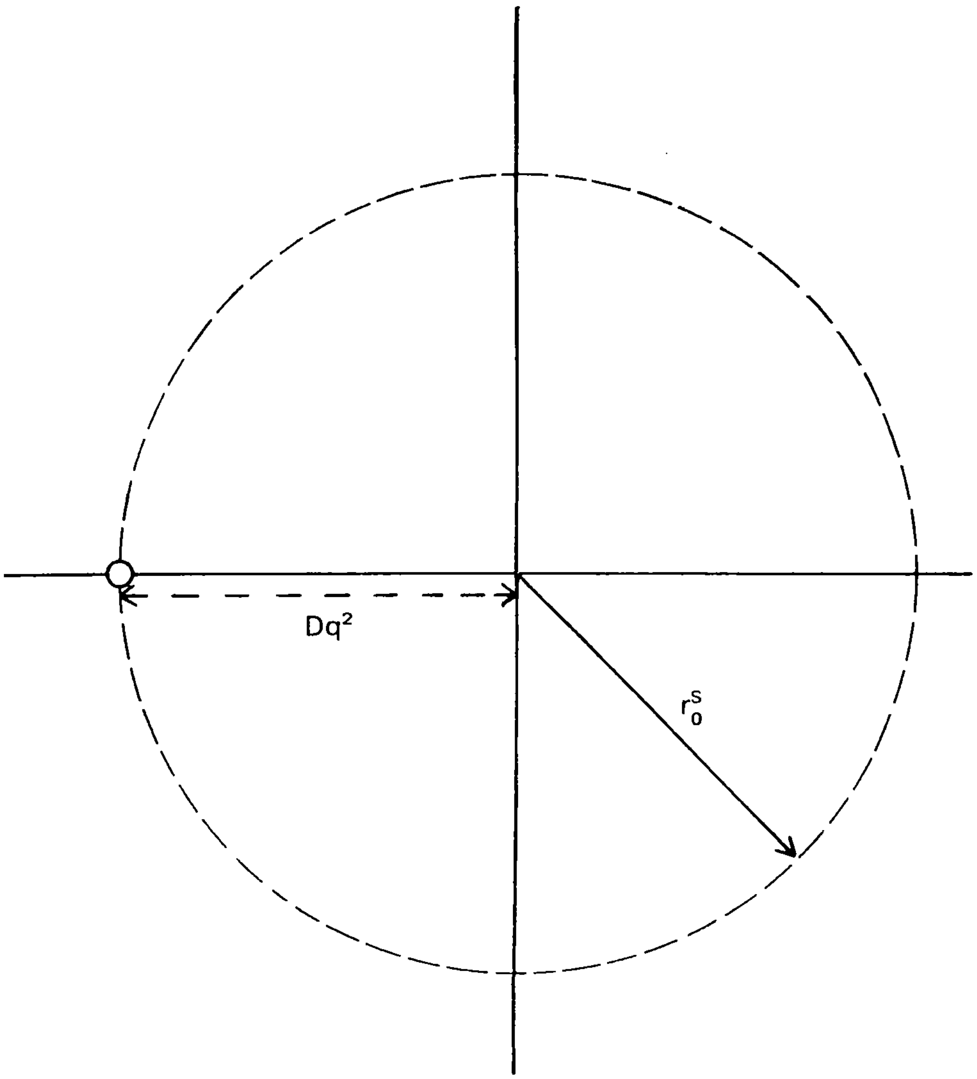

Figure 2.

result, we can approximately relate the radius of convergence of this new series to the transport coefficient Γ.

The basis of the present method lies in the fact that both $\chi(q, p)$ and $\chi_s(q, p)$ are monotonically decreasing positive real functions of p. For a general response function, this assertion was proved by N. N. Meiman and is discussed at length by Landau and Lifshitz.[5] The proof relies only on the general principles of causality and thermodynamic stability, plus certain theorems in the theory of analytic functions, and can be taken over immediately to $\chi(q, p)$ and $\chi_s(q, p)$.

Since $\chi_s(q, p)$ is a monotonically decreasing function of p, it has an inverse $\chi_s^{-1}(\chi_s) = p$, which is single-valued. Hence we may write

$$\chi(q, p) = \chi(q, \chi_s^{-1}(\chi_s)) = \hat{\chi}(q, \chi_s(qp)). \tag{4.1}$$

It must be emphasized that $\hat{\chi}(q, \chi_s)$ is a complicated function depending on the functional form of $\chi_s(qp)$. Nevertheless, it may be expanded about $\chi_s = 0$ and the desired series results, namely

$$\chi = \sum_{n=1}^{\infty} a_n \chi_s^n(qp). \tag{4.2}$$

That the series (4.2) converges for some finite range of χ_s about $\chi_s = 0$ may be seen as follows. Since $\chi_s(qp)$ has an expansion about $p \to \infty$ where $\chi_s = 0$, by the implicit function theorem it follows that χ_s^{-1} has an expansion about $\chi_s = 0$, where $\chi_s^{-1} \to \infty$. Furthermore, since we know that $\chi(q, \chi_s^{-1})$ has an expansion about $\chi_s^{-1} \to p \to \infty$ it is certain that $\hat{\chi}(q, \chi_s)$ must have a small χ_s expansion that converges in some finite interval $0 \leqslant \chi_s \leqslant R_0$.

Having established the existence of the expansion (4.2), we must now turn to the calculation of the coefficients a_n. By substituting the moment expansions (2.5) and (2.6) into Eq. (4.2), we obtain immediately

$$\begin{aligned} \chi(qp) &= \sum_{n=1}^{\infty} \alpha_n \left(\frac{1}{p^2}\right)^n = \sum_n a_n \chi_s^n \\ &= \sum_{n=1}^{\infty} a_n \left[\sum_{m=1}^{\infty} \gamma_m \left(\frac{1}{p^2}\right)^m\right]^n. \end{aligned} \tag{4.3}$$

Formally we can write

$$\left[\sum_{m=1}^{\infty} \gamma_m \left(\frac{1}{p^2}\right)^m\right]^l = \sum_{m=0}^{\infty} c_m{}^l \left(\frac{1}{p^2}\right)^{l+m} \tag{4.4}$$

where

$$c_0{}^l = \gamma_1{}^l \tag{4.5}$$

and

$$c_m{}^l = \frac{1}{m\gamma_1} \sum_{k=1}^{m} (lk - m + k)\gamma_{k+1} c_{m-k}^l \, . \tag{4.6}$$

Therefore, by equating coefficients of various powers of $1/p^2$ in (4.3), we may write

$$\alpha_n = \sum_{l=1}^{\infty} \sum_{m=0}^{\infty} a_l c_m{}^l \delta_{l+m,\,n} = \sum_{l=1}^{\infty} a_l c_{n-l}^l . \tag{4.7}$$

Thus, by solving (4.6) for the coefficients $c_m{}^l$ in terms of the γ_n's and substituting the result in (4.7) an infinite set of algebraic equations is obtained for the a_n's in terms of the α_n's and γ_n's, which are respectively, the moments of the coherent and incoherent scattering functions $S(q\omega)$ and $S_s(q\omega)$. Having solved these equations, we have accomplished the task of generating an expansion of χ in terms of χ_s. It should be stressed that this expansion is exact in the sense that it gives χ exactly provided the assumptions of causality and thermodynamic stability hold, and $\chi_s < R$, the radius of convergence.

To make the argument quite concrete, let us calculate the first few coefficients in our new expansion. From Eqs. (4.5) and (4.6) we have

$$\begin{aligned} &c_0{}^1 = \gamma_1, \qquad c_0{}^2 = \gamma_1{}^2, \qquad c_0{}^3 = \gamma_1{}^3 \\ &c_1{}^1 = \gamma_2, \qquad c_1{}^2 = 2\gamma_1\gamma_2, \\ &c_2{}^1 = \gamma_3. \end{aligned} \tag{4.8}$$

From Eq. (4.7) we have further

$$\begin{aligned} \alpha_1 &= a_1 c_0{}^1 \\ \alpha_2 &= a_1 c_1{}^1 + a_2 c_0{}^2 \\ \alpha_3 &= a_1 c_2{}^1 + a_2 c_1{}^2 + a_3 c_0{}^3 \end{aligned} \tag{4.9}$$

and hence we find

$$\begin{aligned} a_1 &= 1 \\ a_2 &= \frac{\alpha_2 - \gamma_2}{(\gamma_1)^2} \\ a_3 &= \frac{\alpha_3 - \gamma_3}{(\gamma_1)^3} - 2\frac{\alpha_2 - \gamma_2}{(\gamma_1)^4}\gamma_2 . \end{aligned} \tag{4.10}$$

Explicit expressions for α_n and γ_n, $n = 1$ to 3 inclusive, are known in terms of the static correlation functions and the pair potential. Though very tedious, there is no difficulty in principle in calculating the higher order coefficients.

5. Radius of Convergence of χ–χ_s Expansion and Transport Coefficient

We again have recourse to the fact that the high order coefficients in a power series like (4.2) are almost entirely determined by the behaviour of the function represented by the series, near its singularities. We have already seen what the nature of the singularities of χ is in the hydrodynamic regime, from Eq. (3.1).

As before, we note that the radius of convergence R of the series (4.2) is given by

$$\lim_{n\to\infty}\left|\frac{a_{n+1}}{a_n}\right| = \frac{1}{R}, \tag{5.1}$$

provided this limit exists. The question we must then answer concerns the position of the poles of χ in the complex χ_s plane. To find out this information, we note that χ blows up at the diffusion pole $z = -Dq^2$. However, it does so because χ_s goes to infinity, and since (4.2) is a series with a finite radius of convergence R, this singularity is of no interest to us.

Our interest is therefore in the sound wave poles which we have seen to be at $z = z_0^{\pm}$. Clearly, χ_s is finite here, and such that

$$\chi_s(qz_0^{\pm}) \equiv \xi_0^{\pm}. \tag{5.2}$$

Hence the function $\sum a_n \xi^n = \chi(q\xi)$ must have a pole in the complex plane when $\xi = \xi_0^{\pm}$. Therefore, in complete analogy with the discussion in Sec. 3, we may conclude that

$$\lim_{n\to\infty}\left|\frac{a_{n+1}}{a_n}\right| = \frac{1}{R} = \frac{1}{\sqrt{\xi^+\xi^-}} = \frac{1}{|\xi^+|} = \frac{1}{|\xi^-|} \tag{5.3}$$

where we have used the fact that $\chi_s(pz^*) = \chi_s^*(pz)$, since χ_s is analytic. For sufficiently small q, χ_s is well described by the hydrodynamic form given by Eq. (3.8). Thus we find

$$\lim_{n\to\infty}\frac{a_{n+1}}{a_n} = \sqrt{\frac{(z_0^+ + Dq^2)(z_0^- + Dq^2)}{(\beta Dq^2)^2}} = \sqrt{\frac{D(D-2\Gamma)q^4 + \omega_q^2}{\beta^2 D^2 q^4}}. \tag{5.4}$$

Calculating the limit on the left-hand-side of Eq. (5.4) and then solving for Γ, we obtain the result

$$\Gamma = \lim_{q\to 0}\left[\frac{D}{2}+\frac{1}{2D}\left(\frac{v_s^2}{q^2}-\beta^2 D^2 L^2(q)\right)\right] \tag{5.5}$$

where

$$L(q) = \lim_{n\to\infty}\left|\frac{a_{n+1}(q)}{a_n(q)}\right| = \frac{1}{R(q)}. \tag{5.6}$$

Equation (4.2), which is exact, is the main result of this paper. Equation (5.5) is an expression relating the sound wave attenuation Γ to the diffusion coefficient D, the velocity of sound v_s, and the moments α_n and γ_n. This is the alternative we are proposing to the Kubo formula (1.6): we are not able to show it is exact and it may be necessary to use it only for small n.

We wish to point out here that the presence of the diffusion coefficient D in (5.5) is specially due to our choice of χ_s as a new expansion variable. Had we chosen another monotonically decreasing function of p, like $(1/1+p)$ say, then by an analogous argument we would obtain an alternative relation for Γ.

To see the basic point involved, we refer to Fig. 1. Evidently, it is the symmetrical positions of the poles $z_0{}^{\pm}$ which prevents us getting an expression for Γ, assuming a priori knowledge of the velocity of sound v_s. Hence, any transformation of the variable p, or rather a mapping of z to another complex plane ξ, which removes this symmetry, will give us the desired result.

The reason why $\chi_s(q, p)$ was chosen as the expansion variable, in spite of the added calculational complexity, is that the expansion in χ_s allows us to make direct contact with earlier theories of dynamical response in simple liquids, and to relate coherent and incoherent neutron scattering.

6. Approximate Theories

A number of approximate theories exist which express the response of a simple liquid to an external perturbation in terms of the meanderings of a randomly selected atom. The results of these theories are summarized in Table 1, where they are written as relations between χ and χ_s.

B

TABLE 1

Vineyard (6)	$\chi(qp) = S(q)\chi_s(qp)$
Kerr (7)	$\chi(qp) = \dfrac{\chi_s(qp)}{1 - \beta c(q)\chi_s(qp)}$
Hubbard and Beeby (4)	$\chi(qp) = \dfrac{-pq^2}{M}\dfrac{(\chi_s/Dq^2\beta)^2}{1+\omega_q^2(\chi_s/Dq^2\beta)^2}$

NOTE: $S(q)$ is the liquid structure factor while $c(q)$ is the direct correlation function defined as $[S(q)-1]/S(q)$. To write the Hubbard–Beeby result in the above form, use has been made of the hydrodynamic form of χ_s given by Eq. (3.8).

Clearly, all three results can be written as expansions of χ in powers of χ_s. By comparing these expansions with (4.2), a set of approximate a_n's may be obtained. One can then attempt to evaluate the transport coefficient Γ from (5.5).

Vineyard's theory, which was historically the first to relate χ and χ_s is evidently too simple. It predicts an infinite radius of convergence and, as is well known, it misses out the sound wave poles altogether.

In the case of Kerr's theory (his simplified model in which the fourth moment is violated; though his general theory does not suffer from this defect) a finite radius of convergence exists, given by $L(q) = 1/\beta c(q)$, but it remains finite as q tends to zero, whereas Eq. (5.5) would require that $L^2(q)$ should have a q^{-2} singularity as $q \to 0$. The conclusion is again that it is still too simple a theory to describe correctly a hydrodynamic pole.

The Hubbard–Beeby theory involves only even powers of χ_s in the hydrodynamic limit as seen from Table 1, and hence one must calculate the radius of convergence from the formula

$$\lim_{n\to\infty} \frac{a_{n+2}}{a_n} = L^2(q) \tag{6.1}$$

which then gives

$$L^2(q) = \frac{\omega_q^2}{(Dq^2\beta)^2}. \tag{6.2}$$

It then follows from Eq. (5.5) that

$$\Gamma = \frac{D}{2}, \qquad v_s = \lim_{q\to 0}\frac{\omega_q^2}{q^2}. \tag{6.3}$$

It is reassuring to note that the above conclusions about the approximate theories arrived at from our approximation for calculating transport coefficients are the same as those drawn by the present writers[8] by using the Kubo formulae.

7. Relation of χ–χ_s Expansion to Neutron Scattering

What lends impetus to formulating theories that relate $\chi(qp)$ to $\chi_s(qp)$ is the fact that both of these response functions can be measured independently by suitable neutron experiments. Thus, the scattering function $S(q\omega)$ is directly related to the probability that a neutron impinging on the liquid will transfer a momentum $\hbar q$ and an energy $\hbar\omega$ to the liquid. $S_s(q\omega)$ can be studied by measuring the incoherent scattering. Now the fluctuation dissipation theorem relates $S_s(q\omega)$ to Im $\chi_s(q - i\omega)$ and $S(q, \omega)$ to Im $\chi(q, -i\omega)$. This knowledge, in turn, is, at least in principle, sufficient to determine χ_s and χ through the Kramers–Kronig relation. Thus neutron scattering experiments can be thought of as directly determining χ and χ_s.

Now in the approximate theories listed in the previous section, it is fair to say that the self response function χ_s appears in the course of the approximations made for χ; that is essentially "accidentally".

As regards the main purpose of this paper, the question as to whether χ can be exactly related to χ_s is answered in the affirmative in Sec. 4. Admittedly, the relation we propose is a very complicated one, for the coefficients a_n are functionals of χ and χ_s. Nevertheless, it shows that the philosophy of Vineyard (1958) is completely justified and offers promise of basically relating the incoherent and coherent neutron scattering from liquids.†

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† Some detailed numerical consequences of Eq. (4.2) for specific liquids will be reported elsewhere by Dr. M. I. Barker and one of us (N. H. M.), together with work on the analytic structure of the $\chi - \chi_s$ relation.

of the response functions. We also acknowledge support for this work from the Science Research Council.

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