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Hydrodynamic Equations and Correlation Functions

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The response of a system to an external disturbance can always be expressed in terms of time dependent correlation functions of the undisturbed system. More particularly the linear response of a system disturbed slightly from equilibrium is characterized by the expectation value in the equilibrium ensemble, of a product of two space- and time-dependent operators. When a disturbance leads to a very slow variation in space and time of all physical quantities, the response may alternatively be described by the linearized hydrodynamic equations. The purpose of this paper is to exhibit the complicated structure the correlation functions must have in order that these descriptions coincide. From the hydrodynamic equations the slowly varying part of the expectation values of correlations of densities of conserved quantities is inferred. Two illustrative examples are considered: spin diffusion and transport is an ordinary one-component fluid.

Since the descriptions are equivalent, all transport processes which occur in the nonequilibrium system must be exhibited in the equilibrium correlation functions. Thus, when the hydrodynamic equations predict the existence of a diffusion process, the correlation functions will include a part which satisfies a diffusion equation. Similarly when sound waves occur in the nonequilibrium system, they will also be contained in the correlation functions.

The description in terms of correlation functions leads naturally to expressions for the transport coefficients like those discussed by Kubo. The analysis also leads to a number of sum rules relating the dissipative linear coefficients to thermodynamic derivatives. It elucidates the peculiarly singular limiting behavior these correlations must have.

I. INTRODUCTION

Although the general nonequilibrium behavior of a many-particle system is exceedingly complex, there exists a well-developed—and relatively simple—theory

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of nonequilibrium behavior for situations in which physical quantities vary extremely slowly in space and time. The best known example of such a theory is ordinary fluid mechanics. The full nonequilibrium problem involves virtually infinite complexity; on the other hand, the hydrodynamical limit is simply characterized by five partial differential equations.[1]

The simplification occurs because when all physical quantities vary slowly in space and time each portion of the system is almost in thermodynamic equilibrium. Under these conditions, the variation in the system is completely described by local values of the various thermodynamic variables—for example, by giving the pressure, density, and velocity as a function of space and time. The basis of fluid mechanics is the partial differential equations satisfied by these local thermodynamic quantities.

In these hydrodynamic equations, there appear a variety of parameters whose values are not given by fluid mechanics. These parameters fall into two categories. First, there are the thermodynamic derivatives which arise because changes in the various local variables are related by thermodynamic identities. Second, there are the transport coefficients like viscosity and thermal conductivity which enter because the fluxes of thermodynamic quantities contain terms proportional to the gradients of the local variables. To find the values of the transport coefficients and thermodynamic derivatives, we must turn to a more fundamental theory than fluid mechanics.

Recently, it has been appreciated that time-dependent correlation functions afford a powerful theoretical tool for investigating nonequilibrium behavior. Indeed a wide variety of nonequilibrium phenomena are described by thermodynamically averaged expectation values of products of pairs of densities of conserved quantities at different space-time points. In particular these correlation functions completely describe the nonequilibrium behavior of a system in which the deviation from equilibrium is small. Since, in principle, we know how to compute these equilibrium-averaged [2, 3] time-dependent correlation functions, we are in principle able to completely determine the behavior of a system slightly disturbed from equilibrium. Specifically, a calculation of the time dependent correlation functions must lead both to the hydrodynamic equations and the numerical values of all the thermodynamic derivatives and transport coefficients.

In practice the computational difficulties involved in evaluating correlation functions are nontrivial. Indeed, the part of the correlation function which varies slowly in space and time and reflects the hydrodynamic equations is the most difficult part to compute.

The reason for this difficulty is easy to see. The hydrodynamic equations refer to a system in local thermodynamic equilibrium. This local equilibrium is produced and enforced by the frequent collisions between particles.[2] So, the hydrodynamic equations refer to a situation in which the behavior of the system is dominated by

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[1] This simplification is called a contraction of the description. It is discussed in Ref. [1].

[2] A description of how this occurs is given in Ref. [1] and also in Ref. [4].

collisions. On the other hand, the conventional methods [2, 3] for computing correlation functions are based, in one sense or another, on an expansion in some parameter describing the number of collisions in the system. This parameter is most often the strength of the interparticle potential. Since the hydrodynamic equations only appear when the behavior is dominated by the secular effects of collisions, the most straightforward techniques for determining the correlation functions cannot be successfully applied to the prediction of hydrodynamic phenomena.[3]

In this paper, which is largely pedagogical, we shall be primarily concerned with using the hydrodynamic equations to learn about the correlation functions. Our analysis will bear on the inverse problem, the derivation of the hydrodynamical equations, mainly in a negative way. We shall see that the correlation functions must exhibit complicated singular behavior at long wavelengths and low frequencies. This behavior, which does not result in each order of perturbation theory, indicates the necessity for determining successive approximations through iterative integral equations or equivalently through extensive resummation of perturbation expansions.

We first consider the simplest example of a transport process: spin diffusion. In this case the only hydrodynamic equation is a diffusion equation for the spin magnetization. From this hydrodynamic equation, we determine the form of the slowly varying part of the magnetization–magnetization correlation function. The hydrodynamic description which involves the spin susceptibility (a thermodynamic derivative) and the spin diffusion coefficient (a transport coefficient) enters into the correlation function. By comparing this result with the correlation function description we find how the correlation function determines both the thermodynamic derivative and the transport coefficient.

A very similar type of analysis is applied to the algebraically more complex case of transport in a single component fluid. Here, the linearized form of the usual equations of fluid mechanics serve as the hydrodynamic equations. The form of the correlation functions composed of the densities of conserved operators (number, energy, and momentum) are again determined from these hydrodynamic equations. In particular, it is shown how the correlation functions yield the various thermodynamic derivatives and the formulas discussed by Kubo [6] and many other people [7] for the relevant transport coefficients: the viscosity, the bulk viscosity, and the thermal conductivity.

The expressions derived are useful in calculating quantities which appear in the transport equations. They are also interesting for the converse purpose. The correlation functions themselves are of direct experimental interest. Inelastic neutron scattering, for example, directly measures the density–density correlation function [8]. By incorporating information about the form of the correlation function and the thermodynamic derivatives and transport coefficients which occur in it, we may attempt to interpret this kind of experimental data [9]. In fact, a similar but more heuristic analysis [10] is already in use in this connection.

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[3] One possible correlation function approach has been discussed by Baym and Kadanoff [5].

II. SPIN DIFFUSION

A. *Hydrodynamic Description*

As a concrete example of the simplest kind of transport process possible we consider a fluid composed of uncharged particles with spin 1/2. The particles interact through a velocity- and spin-independent force. This situation is realized to an excellent approximation in at least one system of current interest, liquid He^3.

In describing spin transport, we choose a specific direction of spin quantization. If, at a given point in space, the spin of the particles was just as likely to point antiparallel to the direction of quantization as parallel to it, the spin magnetization would vanish there. However, if there were an imbalance between the densities of particles pointing in the two directions, there would be a magnetization proportional to the difference in densities. We shall represent the magnetization in the direction of quantization at the space-time point $\mathbf{r}$, t by the symbol $M(\mathbf{r}, t)$.

An essential feature of the discussion of spin transport will be the assumption that the total magnetization is conserved, that is,

$$\frac{d}{dt}\int d\mathbf{r} M(\mathbf{r}, t) = 0. \tag{1}$$

This neglects, for example, any coupling of the electron spins with magnetic impurities or nuclear spins. The conservation law (1) follows from the fact that the total magnetization is proportional to the total spin of the entire system, and this total spin is a constant of the motion. The conservation law also has a differential form, a continuity equation for the magnetization

$$\frac{\partial}{\partial t} M(\mathbf{r}, t) + \nabla \cdot \mathbf{j}^M(r, t) = 0. \tag{2}$$

Here, $\mathbf{j}^M(\mathbf{r}, t)$ is the magnetization current. We can write expressions for these quantities in terms of the quantum mechanical operators which describe the individual particles in the system. Let the νth particle have position $\mathbf{r}_\nu(t)$, momentum $\mathbf{p}_\nu(t)$, and spin in the direction of quantization $s_\nu(t)$. Let m and γ be the mass and spin magnetic moment of all the particles. Then, the magnetization and magnetization currents are given by

$$\begin{aligned} M(\mathbf{r}, t) &= \sum_\nu \gamma s_\nu(t)\, \delta(\mathbf{r} - \mathbf{r}_\nu(t)) \\ \mathbf{j}^M(\mathbf{r}, t) &= \sum_\nu \gamma s_\nu(t) \{\mathbf{p}_\nu(t), \delta(\mathbf{r} - \mathbf{r}_\nu(t))/2m\}. \end{aligned} \tag{3}$$

Here, the curly brackets represent the anticommutator

$$\{A, B\} = AB + BA.$$

For this system the hydrodynamic equation is extremely simple. When all the properties of the system vary slowly in space and time[4]

$$\langle \mathbf{j}^M(\mathbf{r}, t)\rangle = -D\nabla\langle M(\mathbf{r}, t)\rangle. \tag{4}$$

The transport coefficient, D, is called the spin diffusion coefficient. By combining (2) and (4), we get a diffusion equation for the magnetization,

$$\frac{\partial}{\partial t}\langle M(\mathbf{r}, t)\rangle = D\nabla^2\langle M(\mathbf{r}, t)\rangle. \tag{5}$$

So far, we have not asked about how the system came to be disturbed from full thermodynamic equilibrium. Of course, Eq. (5) is correct, whenever the variation in space and time is sufficiently slow, independent of the type of initial disturbance. Nevertheless, it is useful for us to consider a specific mechanism for producing the deviation from equilibrium.

The simplest such mechanism is a magnetic field $H(\mathbf{r}, t)$ pointing in the direction of quantization. Let us suppose that a spatially varying magnetic field has been adiabatically applied and is suddenly turned off at time $t=0$, so that

$$\begin{aligned} H(\mathbf{r}, t) &= H(\mathbf{r})\, e^{\epsilon t} \qquad && t<0 \\ &= 0 && t>0, \end{aligned} \tag{6}$$

where ϵ is an infinitesimal positive number. Of course, a magnetic field which is independent of time and varies slowly in space will induce a magnetization of the form

$$\langle M(\mathbf{r})\rangle = \chi H(\mathbf{r}). \tag{7}$$

The coefficient, χ, is called the spin susceptibility. It is the thermodynamic derivative

$$\chi = \left.\frac{\partial M}{\partial H}\right|_{H=0}. \tag{8}$$

Now, we have a complete description of the response to the disturbance (6). While the magnetic field is applied, the magnetization must satisfy (7); after it is turned off, $M(\mathbf{r}, t)$ will satisfy (5). In order to represent the relaxation behavior in a convenient form, we define a quantity $M(\mathbf{k}, z)$ which is the Fourier transform of

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[4] This relation was first proposed by Bloembergen [11a] for spins on nuclei fixed on a lattice. See also [11b]. It was derived for particles which are free to move by Torrey [11c] and also by Hart [11d].

the induced magnetization in space and effectively the Laplace transform in time. That is, we write

$$M(\mathbf{k}, z) = \int d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} \int_0^\infty dt e^{izt} \langle M(\mathbf{r}, t) \rangle. \tag{9}$$

In Eq. (9), z is a complex number. It must lie in the upper half of the complex plane for the time integral to converge.

It is quite easy to calculate $M(\mathbf{k}, z)$. We perform the transformation indicated in (9) upon (5), finding

$$0 = \int d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} \int_0^\infty dt e^{izt} \left[\frac{\partial}{\partial t} \langle M(\mathbf{r}, t) \rangle - D\nabla^2 \langle M(\mathbf{r}, t) \rangle \right].$$

After this equation is integrated by parts, it becomes

$$0 = \int d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} \int_0^\infty dt e^{izt} (-iz + Dk^2) \langle M(\mathbf{r}, t) \rangle - \int d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} \langle M(\mathbf{r}, 0) \rangle.$$

According to (7), the spatial Fourier transform of the magnetization at time zero is χ times the Fourier transform of the magnetic field. Thus, we have

$$0 = (-iz + Dk^2)\, M(\mathbf{k}, z) - \int d\mathbf{r} \chi H(\mathbf{r})\, e^{-i\mathbf{k}\cdot\mathbf{r}}.$$

We use the symbol $H(\mathbf{k})$ to denote the Fourier transform of the magnetic field at time zero and find

$$M(\mathbf{k}, z) = \frac{\chi H(\mathbf{k})}{-iz + Dk^2}. \tag{10}$$

Equation (10) is a simple representation of the information contained in the hydrodynamic equations for spin diffusion. Notice that the existence of a diffusion process is reflected in the pole in (10) at $z = -iDk^2$.

We shall use the evaluation (10) of $M(\mathbf{k}, z)$ to determine the magnetization–magnetization correlation function.

B. *Correlation Function Description*

In order to develop the correlation function description of spin diffusion, we notice that an external magnetic field can be represented by an extra time-dependent term added to the Hamiltonian of the system

$$\delta\mathscr{H}(t) = -\int d\mathbf{r} M(\mathbf{r}, t)\, H(\mathbf{r}, t). \tag{11}$$

According to the standard techniques of quantum mechanical perturbation theory, the linear change in the average of any operator, $A(\mathbf{r}, t)$, induced by an extra term in the Hamiltonian is

$$\delta\langle A(\mathbf{r}, t)\rangle = -i\int_{-\infty}^{t} dt'\langle[A(\mathbf{r}, t), \delta\mathscr{H}(t')]\rangle_{\text{eq.}}. \tag{12}$$

Equation (12) applies to a system which was in complete thermal equilibrium at time minus infinity; the expectation value on the right hand side, $\langle\ \rangle_{\text{eq.}}$, is the expectation value in the equilibrium ensemble. This result is discussed in some detail in Appendix A.

We apply (12) to a discussion of the induced magnetization by using the change in the Hamiltonian given by (6) and (11). The induced magnetization is given by

$$\begin{aligned}\langle M(\mathbf{r}, t)\rangle &= i\int_{-\infty}^{t} dt' e^{\epsilon t'}\int d\mathbf{r}' H(\mathbf{r}')\langle[M(\mathbf{r}, t), M(\mathbf{r}', t')]\rangle_{\text{eq.}} \qquad t \leqq 0,\\ &= i\int_{-\infty}^{0} dt' e^{\epsilon t'}\int d\mathbf{r}' H(\mathbf{r}')\langle[M(\mathbf{r}, t), M(\mathbf{r}', t')]\rangle_{\text{eq.}} \qquad t \geqq 0.\end{aligned} \tag{13}$$

In order to compare (13) with the result of our hydrodynamic discussion, we introduce an integral representation for the commutator of the magnetization at different space-time points. Because of the space-time translational invariance of the equilibrium system we may write

$$\langle[M(\mathbf{r}, t), M(\mathbf{r}', t')]\rangle_{\text{eq.}} = \int \frac{d\omega}{\pi}\int \frac{d\mathbf{k}}{(2\pi)^3}\chi''(\mathbf{k}, \omega)\, e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}') - i\omega(t-t')}. \tag{14}$$

We shall call $\chi''(\mathbf{k}, \omega)$ the absorptive part of the dynamic susceptibility. Because of the rotational invariance of the system, $\chi''(\mathbf{k}, \omega)$ depends only upon the magnitude of **k**—not its direction. Because $M(\mathbf{r}, t)$ is a Hermitian operator, $\chi''(k, \omega)$ is real and an odd function of the frequency, ω.

Equation (13) now becomes

$$\langle M(\mathbf{r}, t)\rangle = \int \frac{d\mathbf{k}}{(2\pi)^3} H(\mathbf{k})\, e^{i\mathbf{k}\cdot\mathbf{r}}\int \frac{d\omega}{\pi}\frac{\chi''(k, \omega)}{\omega} \qquad \text{for} \quad t \leqq 0, \tag{15}$$

$$= \int \frac{d\mathbf{k}}{(2\pi)^3} H(\mathbf{k})\, e^{i\mathbf{k}\cdot\mathbf{r}}\int \frac{d\omega}{\pi}\frac{\chi''(k, \omega)}{\omega} e^{-i\omega t} \qquad \text{for} \quad t \geqq 0. \tag{16}$$

We convert Eq. (16) into an expression for $M(\mathbf{k}, z)$ by employing the definition (9) of this Laplace–Fourier transform. In this way we find

$$M(\mathbf{k}, z) = \int \frac{d\omega'}{\pi i}\frac{\chi''(k, \omega')}{\omega'(\omega' - z)} H(\mathbf{k}). \tag{17}$$

Equation (10) gives an expression for $M(\mathbf{k}, z)$ which is appropriate in the limit of small k; Eq. (17) gives an expression for $M(\mathbf{k}, z)$ in terms of $\chi''(k, \omega)$. We can therefore solve for $\chi''(k, \omega)$ in the long wavelength limit. We notice that when $\chi''(k, \omega')$ is a smooth function of ω', we can use the identity

$$\lim_{\epsilon \to 0} \frac{1}{\omega' - \omega - i\epsilon} = \mathscr{P} \frac{1}{\omega' - \omega} + \pi i \delta(\omega - \omega'), \tag{18}$$

where $\mathscr{P}$ stands for the principal value. Thus, when z lies just above the real axis, $z = \omega + i\epsilon$,

$$\mathrm{Re}[M(\mathbf{k}, \omega + i\epsilon)/H(\mathbf{k})] = \chi''(k, \omega)/\omega. \tag{19}$$

Equation (10) yields the expression

$$\chi''(k, \omega) = \frac{\chi D k^2 \omega}{\omega^2 + (Dk^2)^2} \cdot \tag{20}$$

Because the hydrodynamic equations are valid for slowly varying disturbances, Eq. (19) gives the correct expression for χ'' at small k. Notice that at long wavelengths and low frequencies the value of $\chi''(k, \omega)$ depends sensitively on the relative magnitude of ω and k^2. When $\omega \ll Dk^2$

$$\chi''(k, \omega) \cong \omega \chi / Dk^2$$

while when $Dk^2 \ll \omega$

$$\chi''(k, \omega) \cong \chi D k^2 / \omega.$$

Equation (20) for the dynamic spin susceptibility contains the same information as the hydrodynamic equations from which it was derived. The fact that the magnetization satisfies a diffusion equation is reflected in the poles of (20) at frequencies $\pm iDk^2$. The magnetization–magnetization commutator deduced from (20) and (14),

$$\langle [M(\mathbf{r}, t), M(\mathbf{r}', t')] \rangle_{\mathrm{eq.}} = -i\chi D \int \frac{d\mathbf{k}}{(2\pi)^3} k^2 e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}') - Dk^2(t-t')} \qquad \text{for} \quad t > t'$$

exhibits this diffusive character.

C. *Sum Rules for* $\chi''(k, \omega)$

So far, we have only made use of $\chi''(k, \omega)$, the absorptive part of the dynamic spin susceptibility. In our further work, it will be convenient to use the complex dynamic susceptibility

$$\chi(k, z) = \int \frac{d\omega'}{\pi} \frac{\chi''(k, \omega')}{\omega' - z}. \tag{21}$$

When z lies just above the real axis $\chi(k, z)$ may be split into its real and imaginary parts

$$\chi(k, \omega+i\epsilon)=\chi'(k, \omega)+i\chi''(k, \omega),$$

the identity (18) yielding

$$\chi'(k, \omega)=\mathscr{P}\int \frac{d\omega'}{\pi}\frac{\chi''(k, \omega')}{\omega'-\omega}. \tag{22a}$$

Equation (22a) is ordinarily called a Kramers–Kronig relation. There are two such relations, which give the real part of the response in terms of the imaginary part and vice versa. The other Kramers–Kronig relation is

$$\chi''(k, \omega)=-\mathscr{P}\int \frac{d\omega'}{\pi}\frac{\chi'(k, \omega')}{\omega'-\omega}. \tag{22b}$$

Equations (22a) and (22b) may be derived from one another by using the relation

$$\mathscr{P}\int \frac{d\bar{\omega}}{\pi}\frac{1}{\omega-\bar{\omega}}\frac{1}{\omega'-\bar{\omega}}=\pi\delta(\omega-\omega').$$

Notice that $M(\mathbf{k}, z)$ can be expressed in terms of $\chi(k, z)$. From (17) we deduce

$$\frac{-izM(\mathbf{k}, z)}{H(\mathbf{k})}=\int \frac{d\omega'}{\pi}\frac{\chi''(k, \omega')}{\omega'}-\chi(k, z)$$

and hence

$$\frac{M(\mathbf{k}, z)}{H(\mathbf{k})}=\frac{-\chi(k, 0)+\chi(k, z)}{iz}. \tag{23}$$

The quantity $\chi(k, 0)$ will prove to be particularly important in all that follows. Its importance is illustrated by taking the Fourier transform of Eq. (15), which gives

$$\begin{aligned} M(\mathbf{k}) &= \int d\mathbf{r}e^{-i\mathbf{k}\cdot\mathbf{r}}\langle M(\mathbf{r}, t=0)\rangle \\ M(\mathbf{k}) &= \int \frac{d\omega'}{\pi}\frac{\chi''(k, \omega')}{\omega'}H(\mathbf{k}) \\ &= \chi'(k, 0)\, H(\mathbf{k}) \\ &= \chi(k, 0)\, H(\mathbf{k}). \end{aligned} \tag{24}$$

Since the response at time zero is a response to an adiabatically applied disturbance, $\chi(k, 0)$ is the static, wave-number dependent, magnetic susceptibility.

Henceforth, we shall use the conventional abbreviation $\chi(k) \equiv \chi(k, 0)$. From (24) we have

$$\chi(k) = \int \frac{d\omega}{\pi} \frac{\chi''(k, \omega)}{\omega}. \tag{25}$$

Equation (24) gives the exact response to an adiabatically magnetic field. However, according to Eq. (7), when the field varies very slowly in space

$$M(\mathbf{k}) = \chi H(\mathbf{k}). \tag{7}$$

Thus, it follows that

$$\chi = \lim_{k \to 0} \chi(k) = \lim_{k \to 0} \int \frac{d\omega}{\pi} \frac{\chi''(k, \omega)}{\omega}. \tag{26}$$

In general, we may view (25) as a sum rule which expresses the static susceptibility in terms of an integral of $\chi''(k, \omega)$. Equation (25) is just an application of one of the Kramers–Kronig relations at zero frequency. In the long wavelength limit, the value of the sum rule is the thermodynamic derivative,

$$\chi = \left. \frac{\partial M}{\partial H} \right|_{H=0}.$$

It is instructive to compare (26) with a more familiar type of sum rule which expresses moments of $\chi''(k, \omega)$ in terms of equal time commutators. The first nontrivial example of this kind of sum rule is obtained by taking the time derivative of Eq. (14) and applying the conservation law (2). This leads to the identity

$$\begin{aligned} \frac{\partial}{\partial t} \langle [M(\mathbf{r}, t), M(\mathbf{r}', t')] \rangle_{\text{eq.}} &= -\langle [\nabla \cdot \mathbf{j}^M(\mathbf{r}, t), M(\mathbf{r}', t')] \rangle_{\text{eq.}} \\ &= -i \int \frac{d\omega}{\pi} \int \frac{d\mathbf{k}}{(2\pi)^3} \omega \chi''(k, \omega)\, e^{i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}') - i\omega(t - t')}. \end{aligned}$$

We can easily compute the equal time commutator of the magnetization and the magnetization current by using the definitions (3) of these quantities and the canonical commutation relations. The result

$$\langle [\mathbf{j}^M(\mathbf{r}, t), M(\mathbf{r}', t')] \rangle_{\text{eq.}} |_{t'=t} = (\gamma^2/4m)\, i \nabla'\, \delta(\mathbf{r} - \mathbf{r}') \langle n(\mathbf{r}, t) \rangle_{\text{eq.}} \tag{27}$$

is a very disguised version of the fundamental statement that the commutator of the position and the momentum is i. Here, $n(\mathbf{r}, t)$ is the density of particles at the space-time point r, t. Equation (27) implies

$$-\int \frac{d\omega}{\pi} \int \frac{d\mathbf{k}}{(2\pi)^3} \omega \chi''(k, \omega)\, e^{i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')} = \frac{\gamma^2 \langle n \rangle_{\text{eq.}}}{4m} \nabla^2\, \delta(\mathbf{r} - \mathbf{r}')$$

or

$$\int \frac{d\omega}{\pi} \omega\chi''(k, \omega) = \frac{n}{m} \frac{\gamma^2}{4} k^2. \tag{28}$$

Equation (28) is the spin analog of the longitudinal *f*-sum rule which has been extensively discussed in the literature. This sum rule is exact for all values of k as is the static Kramers–Kronig relation (25). However the latter has an independently computable thermodynamic value only for small k. The sum rules also differ in that Eq. (28) expresses a moment of χ'' in terms of an equal time commutator while Eq. (25) gives the value of the time integral of a commutator.

These sum rule statements can be incorporated in Eq. (17) for $M(\mathbf{k}, z)/H(\mathbf{k})$ by performing an expansion for large values of z. In particular, Eqs. (23) and (21) may be rewritten as

$$\frac{M(\mathbf{k}, z)}{H(\mathbf{k})} = \frac{i}{z} \chi(k) + \frac{i}{z^2} \int \frac{d\omega}{\pi} \chi''(k, \omega) + \frac{i}{z^3} \int \frac{d\omega}{\pi} \omega\chi''(k, \omega)$$
$$+ \frac{i}{z^3} \int \frac{d\omega}{\pi} \frac{\omega^2}{z - \omega} \chi''(k, \omega). \tag{29}$$

The coefficient of i/z^2 vanishes because $\chi''(k, \omega)$ is an odd function of the frequency. According to the sum rule (27), the coefficient of i/z^3 is $\frac{1}{4} nk^2\gamma^2/m$. Therefore, for small k,

$$\lim_{z \to \infty} \frac{M(\mathbf{k}, z)}{H(\mathbf{k})} = -\frac{\chi}{iz} - \frac{n\gamma^2 k^2}{4iz^3 m} + O\left(\frac{1}{z^4}\right). \tag{30}$$

Using the hydrodynamic equations, we found that for small values of k and z

$$\frac{M(\mathbf{k}, z)}{H(\mathbf{k})} = \frac{\chi}{-iz + Dk^2} \tag{10}$$

and

$$\chi''(k, \omega) = \frac{\chi Dk^2 \omega}{\omega^2 + (Dk^2)^2}. \tag{20}$$

Let us observe now that the hydrodynamic analysis agrees with the sum rule (25) but completely fails to satisfy the rule (28). The easiest way of verifying both properties is to notice that Eq. (10) agrees with Eq. (30) at large values of z only to order i/z.

We might have anticipated that the second sum rule was not satisfied by the expression obtained from the hydrodynamic approximation (10) since that sum rule gives a result of order k^2 while (10) is only expected to be appropriate for the smallest values of k^2. We can understand phenomenologically how the sum rule

(28) is satisfied by extending the hydrodynamic description to include the effect of a collision time.

D. *Introduction of Relaxation Time*

The main reason why the function $\chi''(k,\omega)$ deduced from the hydrodynamic equations fails to satisfy the commutation sum rule can be traced to the assumption that the current responds instantly to changes in the magnetization according to

$$\langle \mathbf{j}^M(\mathbf{r},t)\rangle = -D\nabla\langle M(\mathbf{r},t)\rangle \qquad \text{for} \quad t \geqq 0. \tag{4}$$

Actually, there must be some lag in the response of the magnetic current to rapid changes in the magnetization. Let us suppose that this response lag is described by a single relaxation time, τ, according to the equation

$$\frac{\partial}{\partial t}\langle \mathbf{j}^M(\mathbf{r},t)\rangle = -\frac{1}{\tau}\left[\langle \mathbf{j}^M(\mathbf{r},t)\rangle + D\nabla\langle M(\mathbf{r},t)\rangle\right] \qquad \text{for} \quad t \geqq 0.$$

We may substitute this form for the current into the conservation law and find

$$\left[\frac{\partial^2}{\partial t^2} + \frac{1}{\tau}\left(\frac{\partial}{\partial t} - D\nabla^2\right)\right]\langle M(\mathbf{r},t)\rangle = 0 \qquad \text{for} \quad t \geqq 0. \tag{31}$$

We again find $M(\mathbf{k},z)$ by Laplace transforming in time and Fourier transforming in space the equation of motion. After using the initial conditions

$$\langle M(\mathbf{r},0)\rangle = \chi H(\mathbf{r}) \qquad \frac{\partial}{\partial t}\langle M(\mathbf{r},t)\rangle|_{t=0} = 0$$

we obtain

$$\frac{M(\mathbf{k},z)}{H(\mathbf{k})} = \frac{\chi(1-iz\tau)}{-iz + Dk^2 - \tau z^2}. \tag{32}$$

To see whether (32) agrees with our sum rules, we expand for large z obtaining

$$\frac{M(\mathbf{k},z)}{H(\mathbf{k})} = \frac{i\chi}{z} + \frac{iDk^2\chi}{\tau z^3} + \mathcal{O}\left(\frac{1}{z^4}\right).$$

Hence, all the requirements including (30) can be satisfied by taking a relaxation time which satisfies

$$D = \frac{n\gamma^2}{4m}\frac{\tau}{\chi}. \tag{33}$$

Equation (33) has been used by Hone [12a] to achieve a semiquantitative understanding of the experimental value of D in liquid He^3 at very low temperatures.

It has also been used by Moriya [12b] in discussing the spin correlation function in ferromagnets.

According to Eq. (19), the dynamic susceptibility can be determined as $\mathrm{Re}[M(\mathbf{k}, \omega)/H(\mathbf{k})]\,\omega$. Therefore, from Eqs. (32) and (33) we find in the single collision time approximation

$$\chi''(k, \omega) = \frac{\chi D k^2 \omega}{\omega^2 + D^2[k^2 - (4\omega^2 \chi m/n\gamma^2)]^2}. \tag{34}$$

Also, from (32) and (33) we find

$$\chi(k, z) = \chi + \frac{iM(k, z)\, z}{H(k)} = \chi \left(1 - \frac{iz}{Dk^2} - \frac{4z^2 \chi m}{n\gamma^2 k^2}\right)^{-1}. \tag{35}$$

E. *Dispersion Relation Representations for Susceptibility*

It should be emphasized that Eqs. (34) and (35) are in no sense exact. In this section, we shall generalize the phenomenological discussion in an exact form.

In order to derive this generalization, we first examine the analytic properties of $\chi(k, z)$. We note that $\chi(k, z)$ is an analytic function of the complex variable z whose singularities lie entirely on the real z axis. From Eqs. (35) and (23), we see that, in the constant collision time approximation,

$$\frac{1}{\chi(k, z)} - \frac{1}{\chi} = -\frac{4mz^2}{n\gamma^2 k^2} - \frac{iz}{D\chi k^2}. \tag{36}$$

Consequently, we might guess that the quantity

$$\frac{1}{z^2}\left[\frac{1}{\chi(k, z)} - \frac{1}{\chi(k)}\right] + \frac{4m}{n\gamma^2 k^2}$$

has a relatively simple analytic structure.

To justify this inference we examine the zeros of $\chi(k, z)$. The important observation to be made is that in a thermodynamically stable system the quantity $\omega\chi''(k, \omega)$, which measures the difference between the energy fed into the system and the energy given up, by a weakly applied field, must be positive definite. For a canonical ensemble this positive definiteness may be directly verified by expanding the commutator in terms of matrix elements and using the fluctuation dissipation theorem. Both of these statements are proven in the appendices. Using the oddness of $\chi''(k, \omega)$ we may write

$$\chi(k, z) = \int \frac{d\omega}{\pi} \frac{\omega}{\omega^2 - z^2} \chi''(k, \omega).$$

Consequently, if $z^2 = x + iy$, we have

$$\operatorname{Im}\chi(k, (x+iy)^{1/2}) = \int \frac{d\omega}{\pi} \frac{\omega y}{(\omega^2 - x)^2 + y^2} \chi''(k, \omega).$$

We see that $\operatorname{Im}\chi(k, z)$ only vanishes for real z^2—that is for z either purely real or purely imaginary. Moreover when z^2 is negative $\chi(k, z)$ is real and positive. Thus the only possible zeros of $\chi(k, z)$ appear for real z. Since the zeros of $\chi(k, z)$ are poles of $1/\chi(k, z)$, the only poles of $1/\chi(k, z)$ lie on the real frequency axis. Finally we recall that in the limit of large z

$$\chi(k, z) = -\int \frac{d\omega}{\pi} \frac{\omega}{z^2} \chi''(k, \omega) = -\frac{n\gamma^2 k^2}{4mz^2}.$$

From these properties we deduce the spectral form

$$\frac{1}{z^2}\left[\frac{1}{\chi(k, z)} - \frac{1}{\chi(k)}\right] + \frac{4m}{nk^2\gamma^2} = -\frac{1}{\chi(k)} \int \frac{d\omega}{\pi} \frac{f(k, \omega)}{\omega z(\omega - z)}. \tag{37}$$

To interpret the spectral weight function, $f(k, \omega)$, we compare this result with Eq. (36). In Eq. (36), the variable z is restricted to lie in the upper half of the complex plane. When $z = \omega + i\epsilon$ the spectral representation becomes

$$\frac{\chi(k)}{\chi(k, \omega + i\epsilon)} - 1 = -\frac{4m\omega^2\chi(k)}{n\gamma^2 k^2} - if(k, \omega) - \mathscr{P}\int \frac{d\omega'}{\pi} \frac{f(k, \omega')\,\omega}{\omega'(\omega' - \omega)}. \tag{38}$$

Since $2if(k, \omega)$ is equal to the discontinuity in the function $\chi^{-1}(k, z)$ across the real axis and that discontinuity is imaginary, the function $f(k, \omega)$ is a real odd function of the frequency. If the function ωf was independent of frequency, the last term in Eq. (38) would vanish and Eq. (38) would be identical with Eq. (36) with $f = \omega/Dk^2$. Therefore, it is reasonable to write

$$f(k, \omega) = \omega/D(k, \omega)\, k^2 \tag{39}$$

with the knowledge that in the limit small wave number and very small frequency $D(k, \omega)$ reduces to the spin diffusivity, at least when $\omega^2 \cong -(Dk^2)^2$.

This leads to an exact spectral representation for $\chi(k, z)$

$$\frac{\chi(k, z)}{\chi(k)\, k^2} = \left[k^2 - \frac{4mz^2}{n\gamma^2}\chi(k) + \int \frac{d\omega}{\pi} \frac{z}{z - \omega} \frac{1}{D(k\omega)}\right]^{-1} \tag{40}$$

and, from Eq. (19),

$$\begin{gathered} \chi''(k, \omega) = \frac{\chi(k)\, D(k, \omega)\, k^2\omega}{\omega^2 + [\;]^2} \\ [\;] \equiv D(k, \omega)\, k^2 - \frac{4m\omega^2}{n\gamma^2} D(k, \omega)\,\chi(k) + \mathscr{P}\int \frac{d\omega'}{\pi} \frac{\omega}{\omega - \omega'} \frac{D(k, \omega)}{D(k, \omega')}. \end{gathered} \tag{41}$$

Of course, Eqs. (40) and (41) give only one of many possible spectral representations for the response. The virtue of this particular representation, however, is that the low frequency and low wave number limit of all the quantities appearing on the right hand side of these equations will be regular. This knowledge is quite useful both for theoretically estimating $\chi(k)$ and $D(k, \omega)$ and for interpreting experimental results on $\chi''(k, \omega)$ in terms of χ and D. Note that if the function $D(k, \omega)$ was constant (40) and (41) would be identical with (35) and (34). This gives a precise meaning to the single collision time approximation.

Equations (40) and (41) are easily modified to describe other self-diffusion processes. In our analysis, the spin on the particles just serves as a kind of label. If the label was somewhat different, for example, if the system contained particles painted red and green or identically interacting isotopes, the results would be unaltered.

Another useful representation is obtained by observing that the function

$$-\frac{4z^2m}{nk^2\gamma^2}\frac{\chi(k, z)}{\chi(k)}$$

is analytic off the real axis and approaches unity at infinity. Its logarithm is therefore analytic for complex z and its real part is continuous for real z. It is therefore possible to represent the function as

$$\frac{\chi(k, z)}{\chi(k)} = -\frac{n\gamma^2k^2}{4mz^2}\exp\int\frac{d\omega'}{\pi}\frac{\delta(k, \omega')}{\omega' - z},$$

where δ is a real function. As ω approaches the real axis we find

$$\chi'(k, \omega) + i\chi''(k, \omega) = \lambda(k, \omega)\,\chi(k)\,e^{i\delta(k, \omega)},$$

where

$$\lambda(k, \omega) = -\frac{n\gamma^2k^2}{4m\omega^2}\exp\mathscr{P}\int\frac{d\omega'}{\pi}\frac{\delta(k, \omega')}{\omega' - \omega}.$$

Moreover the discontinuity in $\chi^{-1}(k, z)/\chi^{-1}(k)$ is given by

$$f(k, \omega) = \lambda^{-1}(k, \omega)\sin\delta(k, \omega).$$

This permits us to identify the argument of $\chi^{-1}(k, z)$, that is, δ, as

$$\omega\cot\delta(k, \omega) = Dk^2$$

in a first approximation, and as

$$\omega\cot\delta(k, \omega) = D\left(k^2 - \frac{4\omega^2\chi m}{n\gamma^2}\right)$$

in the next. We might therefore introduce D as the constant term in an effective range expansion.

F. *Expressions Entailing the Fluctuation–Dissipation Theorem*

One may carry the analysis a bit further by employing the fluctuation–dissipation theorem. This theorem relates the canonically or grand canonically averaged commutator and anticommutator of any pair of hermitian operators $A_i(\mathbf{r}, t)$, each of which commutes with the number operator N and transforms in time according to

$$i\dot{A}_i(\mathbf{r}, t) = [\mathscr{H}, A_i(r, t)].$$

This is to say, the operators are assumed to have no explicit time dependence and the usual implicit time dependence of Heisenberg representation operators. The theorem states that if the commutator of two such operators is given by

$$\langle [A_i(\mathbf{r}, t), A_j(\mathbf{r}', t')] \rangle_{\text{eq.}} \equiv \int \frac{d\omega}{\pi} \int \frac{d\mathbf{k}}{(2\pi)^3} e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}') - i\omega(t-t')} \chi''_{ij}(\mathbf{k}, \omega) \tag{42a}$$

their anticommutator is given by

$$\begin{aligned}&\langle \{A_i(\mathbf{r}, t) - \langle A_i \rangle_{\text{eq.}}, A_j(\mathbf{r}', t') - \langle A_j \rangle_{\text{eq.}}\} \rangle \\ &\quad = \int \frac{d\omega}{\pi} \int \frac{d\mathbf{k}}{(2\pi)^3} e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}') - i\omega(t-t')} \coth \frac{\beta\omega}{2} \chi''_{ij}(\mathbf{k}, \omega).\end{aligned} \tag{42b}$$

This relationship between the commutator and the anticommutator is called a fluctuation–dissipation theorem because the anticommutator expresses the time dependent correlations or fluctuations in the system and, as we have seen, the commutator describes the transport coefficient or dissipation.[5]

In particular, the magnetization anticommutator is

$$\frac{\beta}{2} \langle \{M(\mathbf{r}, t), M(\mathbf{r}', t')\} \rangle = \int \frac{d\omega}{\pi} \int \frac{d\mathbf{k}}{(2\pi)^3} \frac{\beta}{2} \coth \frac{\beta\omega}{2} \chi''(k, \omega)\, e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}') - i\omega(t-t')}. \tag{43}$$

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[5] The fluctuation–dissipation theorem was first derived by Nyquist [13a], who related the random noise in an electrical circuit (the fluctuations) to the response of the circuit to an applied voltage (the dissipation). Callen and Welton [13b] recognized the importance of Nyquist's idea and generalized it somewhat. The fluctuation–dissipation theorem lies at the very heart of much recent work in many particle physics. It is, for example, the "boundary condition" utilized by Martin and Schwinger [2]. For a discussion of the fluctuation–dissipation theorem which is close to the spirit and purpose of this article, see (6).

In the remainder of this section we shall continue to omit the subscripts since we are only considering one operator, the magnetization. From Eq. (20), we see that for large values of r and t, or small values of k and ω, the anticommutator is

$$\frac{\beta}{2}\langle\{M(\mathbf{r},t),M(\mathbf{0},0)\}\rangle_{\text{eq.}}=\chi\int\frac{d\mathbf{k}}{(2\pi)^3}\,e^{i\mathbf{k}\cdot\mathbf{r}-Dk^2|t|}.$$

Therefore, the anticommutator also has a part which satisfies the diffusion equation.

Of course, it is hardly surprising that this correlation function behaves in the same way as a response to an external disturbance. The correlation function reflects how the natural fluctuations in the system die out, while the hydrodynamic equations describe how externally induced deviations from equilibrium disappear. But the system should not really have any way of knowing whether a particular deviation from equilibrium was produced by a natural fluctuation or an external disturbance. Therefore, the same transport processes which appear in the hydrodynamic equations should also manifest themselves in correlation functions.

The fluctuation–dissipation theorem can be used to obtain a frequently quoted expression for the spin diffusion coefficient D. From (20)

$$D\chi=\lim_{\omega\to 0}\left[\lim_{k\to 0}\frac{\omega}{k^2}\chi''(k,\omega)\right].$$

Using (43), $D\chi$ can be expressed in terms of the magnetization anticommutator as

$$D\chi=\lim_{\omega\to 0}\left[\lim_{k\to 0}\int d\mathbf{r}\int dt\,e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')+i\omega(t-t')}\frac{\omega^2}{k^2}\frac{\beta}{4}\langle\{M(\mathbf{r},t),M(\mathbf{r}',t')\}\rangle_{\text{eq.}}\right].$$

The differential conservation law, $(\partial M/\partial t)+\nabla\cdot\mathbf{j}^M=0$, now gives

$$D\chi=\lim_{\omega\to 0}\left[\lim_{k\to 0}\int d\mathbf{r}\int dt\,e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')+i\omega(t-t')}\frac{\beta}{4k^2}\langle\{\mathbf{k}\cdot\mathbf{j}^M(\mathbf{r},t),\mathbf{k}\cdot\mathbf{j}^M(\mathbf{r}',t')\}\rangle\right].$$

Since the direction of $\mathbf{k}$ is now quite irrelevant, we can replace $\mathbf{k}\cdot\mathbf{j}^M/\mathbf{k}$ by, say, the x component of $\mathbf{j}^M$. Thus, we finally find

$$D\chi=\lim_{\omega\to 0}\int d\mathbf{r}\,dt\,e^{i\omega(t-t')}\frac{\beta}{4}\langle\{\mathbf{j}_x{}^M(\mathbf{r},t),\mathbf{j}_x{}^M(\mathbf{r}',t')\}\rangle. \tag{44}$$

This type of expression, in which the transport coefficient is given in terms of the anticommutator of the currents, has been much discussed in the literature [6, 7].

In addition to relating fluctuations to dissipation as in Eqs. (43) and (44) we may use the identity (42) to make another inference. For this purpose we observe that the susceptibility is the thermodynamic derivative,

$$\chi = \left.\frac{\partial M}{\partial H}\right|_{H=0}. \tag{8}$$

For a system in thermal equilibrium in the presence of a static uniform field the magnetization can be calculated in the grand canonical ensemble where the expectation value of any operator is defined by

$$\begin{aligned} \langle A \rangle &\equiv \mathrm{tr}[\rho A] \\ \rho &\equiv \frac{\exp(-\beta[\mathscr{H} - \mu \mathfrak{N}])}{\mathrm{tr}[\exp(-\beta[\mathscr{H} - \mu \mathfrak{N}])]}. \end{aligned} \tag{45}$$

Here, $\mathscr{H}$ and $\mathfrak{N}$, are the Hamiltonian and number operators. The trace is a diagonal sum over all states of the system with all possible values of the energy and the particle number. The parameters μ and β are respectively the chemical potential and the inverse temperature (in energy units).

In calculating the effect of a magnetic field which is independent of r, we apply Eq. (45) to the case in which the Hamiltonian is the Hamiltonian in the absence of the magnetic field, $\mathscr{H}_0$, plus the magnetic energy $-H \int d\mathbf{r} M(\mathbf{r})$. The density matrix ρ can be expanded to first order in the magnetization since the total magnetization commutes with both $\mathscr{H}_0$ and $\mathfrak{N}$. In this manner we obtain

$$\rho \cong \rho_{\text{eq.}} + \rho_{\text{eq.}} \beta H \int d\mathbf{r} \{ M(\mathbf{r}) - \mathrm{tr}[\rho_{\text{eq.}} M(\mathbf{r})] \},$$

where $\rho_{\text{eq.}}$ is the density matrix with no magnetic field

$$\rho_{\text{eq.}} = \frac{\exp(-\beta[\mathscr{H}_0 - \mu \mathfrak{N}])}{\mathrm{tr}[\exp(-\beta[\mathscr{H}_0 - \mu \mathfrak{N}])]}.$$

Since the magnetization must vanish when there is no field,

$$\langle M \rangle = \beta H \, \mathrm{tr}\left[\rho_{\text{eq.}} M(\mathbf{r}) \int d\mathbf{r}' \, M(\mathbf{r}') \right] = \beta H \left\langle M(\mathbf{r}) \int d\mathbf{r}' \, M(\mathbf{r}') \right\rangle_{\text{eq.}},$$

the susceptibility is[6]

$$\frac{\partial M}{\partial H} = \chi = \frac{\beta}{2} \int d\mathbf{r}' \langle \{ M(\mathbf{r}), M(\mathbf{r}') \} \rangle_{\text{eq.}}. \tag{46a}$$

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[6] This expression was first discussed by Kirkwood [14].

(In writing Eq. (46a) we have taken advantage of the fact that, for equal times, the magnetization at one point will commute with the magnetization at another to replace $M(\mathbf{r}')\,M(\mathbf{r})$ by the more symmetrical combination $\frac{1}{2}\{M(\mathbf{r}), M(\mathbf{r}')\}$.) Using the fluctuation–dissipation theorem in the form (43), we may rewrite Eq. (46a) as

$$\chi = \int \frac{d\omega}{\pi} \frac{\beta}{2} \coth \frac{\beta\omega}{2} \chi''(k, \omega)|_{k=0}. \tag{46b}$$

Let us compare this thermodynamic form for the susceptibility with our previous result

$$\chi = \lim_{k \to 0} \int \frac{d\omega}{\pi} \frac{\chi''(k, \omega)}{\omega}. \tag{26}$$

The positive definite integrand in (46b) is greater than or equal to the positive definite integrand of (26) and the two expressions are equal only at $\omega = 0$. It therefore follows that $\chi''(k, \omega)/\omega$ must be very sharply peaked about zero frequency.[7] This sharp peaking of χ''/ω is predicted by Eq. (20) according to which χ''/ω becomes a delta function at zero frequency as k goes to zero. Moreover the integral conservation law

$$\frac{d}{dt} \int d\mathbf{r}\, M(\mathbf{r}, t) = 0$$

implies that the $\mathbf{k} = \mathbf{0}$ part of the anticommutator can only contain zero frequency components. Thus, the frequency integral in (46b) can only contribute at exactly zero frequency and expressions (46b) and (26) are completely consistent with one another.

III. TRANSPORT IN A FLUID

A. *Hydrodynamic Equations*

Spin transport is particularly simple because it is described, in the hydrodynamic limit, by a simple diffusion equation. For most systems, however, the hydrodynamic equations are more complex. This is because there is one transport equation connected with each differential conservation law. For a one-component fluid, for example, there is a conservation law and transport equation for the density of

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[7] There are a few cases known in which the limit as k goes to zero of an integral like (46) is not equal to its value at zero wave number. The most notable example of this pathological behavior is a system of particles interacting through a Coulomb force, in which the long-ranged interaction makes the limit of small wave numbers peculiar.

particles, $n(\mathbf{r}, t)$, the momentum density, $\mathbf{g}(\mathbf{r}, t)$, and the energy density, $\epsilon(\mathbf{r}, t)$. These conservation laws can be written as

$$\frac{\partial}{\partial t} n(\mathbf{r}, t) + \nabla \cdot \mathbf{g}\frac{(\mathbf{r}, t)}{m} = 0 \qquad \text{number conservation,} \tag{47a}$$

$$\frac{\partial}{\partial t} g(\mathbf{r}, t) + \nabla \cdot \tau(\mathbf{r}, t) = 0 \qquad \text{momentum conservation,} \tag{47b}$$

$$\frac{\partial}{\partial t} \epsilon(\mathbf{r}, t) + \nabla \cdot \mathbf{j}^{\epsilon}(\mathbf{r}, t) = 0 \qquad \text{energy conservation.} \tag{47c}$$

Here, j^{ϵ} is the energy current density and τ is the stress tensor, which serves as a momentum current.

Of course Eqs. (47) are incomplete in themselves. They must be supplemented with the assumption that when all variations in space and time are slow, the system can be treated as if it is in thermodynamic equilibrium locally. Since the state of the fluid in equilibrium is characterized by the five conserved variables or five associated intensive variables we expect local equilibrium to be characterized either by the local densities of the conserved variables or by related spatially and temporally varying intensive quantities. Conventionally these are chosen to be the temperature, pressure, and average velocity.

We define an average velocity by writing the momentum density as

$$\langle \mathbf{g}(\mathbf{r}, t)\rangle = \langle n(\mathbf{r}, t)\rangle\, m\mathbf{v}(\mathbf{r}, t).$$

We shall consider the case in which the deviation from complete equilibrium is small. We may further suppose that the complete equilibrium system is taken to be at rest and uniform. We may then write to first order

$$\langle \mathbf{g}(\mathbf{r}, t)\rangle = nm\,\mathbf{v}(\mathbf{r}, t), \tag{48a}$$

where n is the equilibrium density of particles. For a system of particles in complete equilibrium, moving with uniform velocity, $\mathbf{v}$, Galilean invariance implies an energy current

$$\mathbf{j}^{\epsilon} = (\epsilon + p)\,\mathbf{v}.$$

When the system is in local equilibrium the energy current will generally contain a term of this form. However, if there is a temperature gradient in the system, there is an extra flow of energy from hot regions to cold regions. These two effects lead to an energy current of the form

$$\mathbf{j}^{\epsilon}(\mathbf{r}, t) = (\epsilon + p)\,\mathbf{v}(\mathbf{r}, t) - \kappa \nabla T(\mathbf{r}, t), \tag{48b}$$

where ϵ and p are the equilibrium parameters.[8] The coefficient κ is called the thermal conductivity.

Of course, the temperature which appears in (48b) is not independent of the other variables. Because the system is in local thermodynamic equilibrium, variations in the intensive parameters satisfy the usual thermodynamic relations. Thus, a change in the temperature is related to changes in the density and energy density by

$$\nabla T(\mathbf{r}, t) = \left.\frac{\partial T}{\partial n}\right|_{\epsilon} \nabla n(\mathbf{r}, t) + \left.\frac{\partial T}{\partial \epsilon}\right|_{n} \nabla \epsilon(\mathbf{r}, t).$$

To complete the set of equations (48), it is necessary to specify the stress tensor, τ. For a fluid at rest in complete equilibrium the stress tensor takes the form

$$\tau_{ij} = \delta_{ij} p,$$

where p is the pressure. When the fluid is disturbed from equilibrium, extra stresses are produced as a result of viscous forces in the fluid. These forces are proportional to gradients of the velocity so that the full stress tensor may be written as

$$\tau_{ij}(\mathbf{r}, t) = \delta_{ij} p(\mathbf{r}, t) - \eta \left(\frac{\partial v_i(\mathbf{r}, t)}{\partial r_j} + \frac{\partial v_j(\mathbf{r}, t)}{\partial r_i} \right) - \delta_{ij} \nabla \cdot \mathbf{v}(\mathbf{r}, t) \left(\zeta - \frac{2}{3} \eta \right). \tag{48c}$$

Here η is called the viscosity and ζ the second viscosity or bulk viscosity. Again there may be additional terms in a superfluid. We shall henceforth ignore this possibility, restricting ourselves to normal fluids. Changes in the pressure, p, are, in a normal fluid, related to changes in the density, energy density, and temperature through the usual thermodynamic relations. Therefore, Eqs. (47) together with Eqs. (48) form a complete description of the fluid. In fact, they are the linearized form of the usual equations of fluid mechanics.[9]

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[8] However, in a superfluid there exists more general modes of motion than this mode in which the fluid appears locally to be moving as a whole. The superfluid can sustain without appreciable decay the relative motion of its excitations (the normal fluid) against a sea of its condensed state (the superfluid). This extra freedom results in the local equilibrium situation being described by not one but two velocities: the condensed mode velocity v_s and the normal mode velocity v_{n}. In this case, the energy current, neglecting dissipation, is

$$\mathbf{j}^{\epsilon}(\mathbf{r}, t) = (\epsilon + p)\, \mathbf{v}_{\mathrm{n}}(\mathbf{r}, t) + \mu \rho_{\mathrm{s}} (\mathbf{v}_{\mathrm{s}}(\mathbf{r}, t) - \mathbf{v}_{\mathrm{n}}(\mathbf{r}, t)),$$

where ρ_s is the density of the superfluid (condensed) component. The inclusion of this extra degree of freedom of the superfluid changes the hydrodynamic equations and this invalidates all the main conclusions of the present work.

[9] See, for example, Ref. [15].

Now, we recombine these equations in a form which is convenient for our purposes. With the aid of (48a) and (48c), the momentum conservation law may be written as

$$\frac{\partial}{\partial t}\langle \mathbf{g}(\mathbf{r}, t)\rangle + \nabla p(\mathbf{r}, t) - \frac{\eta}{mn}\nabla^2\langle \mathbf{g}(\mathbf{r}, t)\rangle - \frac{\zeta + \frac{1}{3}\eta}{mn}\nabla\nabla\cdot\langle \mathbf{g}(\mathbf{r}, t)\rangle = 0. \tag{49}$$

It is convenient to divide the momentum density into longitudinal and transverse parts, that is, to write

$$\mathbf{g}(\mathbf{r}, t) = \mathbf{g}_l(\mathbf{r}, t) + \mathbf{g}_\mathrm{t}(\mathbf{r}, t),$$

where

$$\nabla\cdot\mathbf{g}_\mathrm{t}(\mathbf{r}, t) = 0$$

$$\nabla\times\mathbf{g}_l(\mathbf{r}, t) = 0.$$

With these definitions, the transverse part of the momentum satisfies the diffusion equation

$$\frac{\partial}{\partial t}\langle \mathbf{g}_\mathrm{t}(\mathbf{r}, t)\rangle = \frac{\eta}{mn}\nabla^2\langle \mathbf{g}_\mathrm{t}(\mathbf{r}, t)\rangle. \tag{50a}$$

To get the remaining hydrodynamic equations, we take the divergence of (49) and use the number conservation law (47a) to eliminate $\mathbf{g}(\mathbf{r}, t)$. We then find

$$\left[-m\frac{\partial^2}{\partial t^2} + \frac{\frac{4}{3}\eta + \zeta}{n}\frac{\partial}{\partial t}\nabla^2\right]\langle n(\mathbf{r}, t)\rangle + \nabla^2 p(\mathbf{r}, t) = 0. \tag{50b}$$

The momentum density may also be eliminated from the energy conservation law which results from substituting (48b) into (47c). In this way, we find

$$\frac{\partial}{\partial t}\left[\langle \epsilon(\mathbf{r}, t)\rangle - \frac{\epsilon + p}{n}\langle n(\mathbf{r}, t)\rangle\right] - \kappa\nabla^2 T(\mathbf{r}, t) = 0. \tag{50c}$$

The analysis of the diffusion equation (50a) follows along exactly the same lines as the analysis of spin diffusion given earlier. We suppose $\mathbf{g}_\mathrm{t}(\mathbf{r}, t)$ dies off at large distances so that we may define

$$\mathbf{g}_\mathrm{t}(\mathbf{k}, z) = \int d\mathbf{r}\int_0^\infty dt\, e^{-i\mathbf{k}\cdot\mathbf{r} + izt}\langle \mathbf{g}_\mathrm{t}(\mathbf{r}, t)\rangle$$

$$\mathbf{g}_\mathrm{t}(\mathbf{k}) = \int d\mathbf{r}\, e^{-i\mathbf{k}\cdot\mathbf{r}}\langle \mathbf{g}_\mathrm{t}(\mathbf{r}, 0)\rangle = mn\,\mathbf{v}_\mathrm{t}(\mathbf{k}).$$

We then find

$$\mathbf{g}_t(\mathbf{k}, z) = \frac{mn\mathbf{v}_t(\mathbf{k})}{-iz + (\eta k^2/mn)}. \tag{51}$$

Equations (50b) and (50c) can be analyzed in a very similar way. We define

$$n(\mathbf{k}, z) = \int d\mathbf{r} \int_0^\infty dt\, e^{-i\mathbf{k}\cdot\mathbf{r} + izt} \langle n(\mathbf{r}, t)\rangle$$

$$p(\mathbf{k}, z) = \int d\mathbf{r} \int_0^\infty dt\, e^{-i\mathbf{k}\cdot\mathbf{r} + izt} p(\mathbf{r}, t)$$

$$n(\mathbf{k}) = \int d\mathbf{r}\, e^{-i\mathbf{k}\cdot\mathbf{r}} \langle n(\mathbf{r}, 0)\rangle, \qquad \text{etc.}$$

We notice that we can guarantee that $\langle \partial n(\mathbf{r}, t)/\partial t\rangle_{t=0} = 0$ by taking the longitudinal part of $v(\mathbf{k})$ to be zero initially. With this additional requirement, the transform of Eqs. (50b) and (50c) become

$$\begin{aligned} &imz(-iz + D_l k^2)\, n(\mathbf{k}, z) - k^2 p(\mathbf{k}, z) \\ &\quad = -m(-iz + D_l k^2)\, n(\mathbf{k}) - iz\left[\epsilon(\mathbf{k}, z) - \frac{\epsilon + p}{n} n(\mathbf{k}, z)\right] + \kappa k^2 T(\mathbf{k}, z) \qquad \text{(52a)} \\ &\quad = -\left[\epsilon(\mathbf{k}) - \frac{\epsilon + k}{n} n(\mathbf{k})\right], \qquad \text{(52b)} \end{aligned}$$

where we have introduced the abbreviation $D_l = (\frac{4}{3}\eta + \zeta)/mn$ for the "longitudinal" diffusion coefficient.

Notice that (52b) involves the quantity

$$q(\mathbf{k}, z) = \epsilon(\mathbf{k}, z) - \frac{\epsilon + p}{n} n(\mathbf{k}, z) \tag{53}$$

which is the change in the energy density minus the enthalpy per particle times the change in the number density. The response $q(\mathbf{k}, z)$ and the corresponding operator,

$$q(\mathbf{r}, t) = \epsilon(\mathbf{r}, t) - \frac{\varepsilon + p}{n} n(\mathbf{r}, t),$$

will play an important role in all that follows. To understand q, we recall the thermodynamic relation

$$TdS = dE + pdV$$

which holds at constant particle number, N. If $dN=0$, we have the additional identities

$$-dV/V=dn/n$$

and

$$dE=d(\epsilon V)=Vd\epsilon+\epsilon dV=V[d\epsilon-(\epsilon/n)\,dn].$$

Thus, at constant N

$$\frac{T}{V}dS=d\epsilon-\frac{\epsilon+p}{n}dn.$$

This permits us to identify $q(\mathbf{r},t)$ as an operator whose changes represent T times the change in the entropy density. Thus, we shall call $q(\mathbf{r},t)$ the density of heat energy.

We are, of course, permitted to use any convenient set of variables in analyzing Eqs. (52). It will prove convenient to use the matter density $n(\mathbf{k},z)$ and the heat energy density $q(\mathbf{k},z)$. Because the system is in local thermodynamic equilibrium the temperature and pressure can be written as[10]

$$T(\mathbf{k},z)=\left.\frac{\partial T}{\partial n}\right|_S n(\mathbf{k},z)+\left.\frac{V}{T}\frac{\partial T}{\partial S}\right|_n q(\mathbf{k},z)$$

$$p(\mathbf{k},z)=\left.\frac{\partial p}{\partial n}\right|_S n(\mathbf{k},z)+\left.\frac{V}{T}\frac{\partial p}{\partial S}\right|_n q(\mathbf{k},z).$$

For the variables which characterize the initial conditions, it is convenient to use not $q(\mathbf{k})$ and $n(\mathbf{k})$ but the pressure and temperature defined by

$$n(\mathbf{k})=\left.\frac{\partial n}{\partial p}\right|_T p(\mathbf{k})+\left.\frac{\partial n}{\partial T}\right|_p T(\mathbf{k})$$

$$q(\mathbf{k})=\left.\frac{T}{V}\frac{\partial S}{\partial p}\right|_T p(\mathbf{k})+\left.\frac{T}{V}\frac{\partial S}{\partial T}\right|_p T(\mathbf{k}).$$

Written in terms of these new variables, (52) becomes

$$\left[izm(-iz+D_l k^2)-k^2\left.\frac{\partial p}{\partial n}\right|_S\right]n(\mathbf{k},z)-k^2\left.\frac{V}{T}\frac{\partial p}{\partial S}\right|_n q(\mathbf{k},z)$$
$$=-m(-iz+D_l k^2)\left[\left.\frac{\partial n}{\partial p}\right|_T p(\mathbf{k})+\left.\frac{\partial n}{\partial T}\right|_p T(\mathbf{k})\right] \qquad (54a)$$

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[10] Because our identification of q was made at fixed N, all the thermodynamic derivatives here and below must be taken at fixed N.

$$\left[-iz+\kappa k^2\frac{V}{T}\frac{\partial T}{\partial S}\bigg|_n\right]q(\mathbf{k},z)+\kappa k^2\frac{\partial T}{\partial n}\bigg|_S n(\mathbf{k},z)$$
$$=\frac{T}{V}\frac{\partial S}{\partial T}\bigg|_p T(\mathbf{k})+\frac{T}{V}\frac{\partial S}{\partial p}\bigg|_T p(\mathbf{k}). \tag{54b}$$

Before discussing the general solution to (54), we consider a particular simplification which occurs at very low temperatures. As the temperature goes to zero the coupling between the mechanical variables (the pressure and the density of particles) and the thermal variables (the temperature and entropy) becomes very weak. The pressure becomes a function of the density not the temperature. Hence the thermodynamic derivatives coupling $q(\mathbf{k},z)$ and $T(\mathbf{k})$ into Eq. (54a) disappear. Similarly, the entropy depends more sensitively on the temperature than on the density or pressure; consequently the thermodynamic derivatives which couple $n(\mathbf{k},z)$ and $p(\mathbf{k})$ into (54b) vanish. In this case the solution to the equations is

$$n(\mathbf{k},z)=-(-iz+D_l k^2)\frac{\partial n}{\partial p}p(\mathbf{k})\left[z^2-\frac{1}{m}\frac{dp}{dn}k^2+izD_l k^2\right]^{-1} \tag{55a}$$

and

$$q(\mathbf{k},z)=\frac{T}{V}\frac{dS}{dT}T(\mathbf{k})\left[-iz+\kappa k^2\frac{V}{T}\frac{dT}{dS}\right]^{-1}. \tag{55b}$$

Equation (55b) states that the temperature satisfies a diffusion equation

$$\frac{\partial}{\partial t}T(\mathbf{r},t)=D_T\nabla^2 T(\mathbf{r},t)$$

for $t>0$, with the thermal diffusivity given by

$$D_T=\kappa\bigg/\frac{T}{V}\frac{dS}{dT}.$$

Equation (55a) states that the density and pressure satisfy a damped sound wave equation

$$\left(\frac{\partial^2}{\partial t^2}-c^2\nabla^2-\Gamma\frac{\partial}{\partial t}\nabla^2\right)p(\mathbf{r},t)=0$$

for $t>0$, with the sound velocity c given by

$$mc^2=dp/dn$$

and the sound wave damping constant

$$\Gamma=D_l.$$

By examining the solutions to Eqs. (54) in the general case, we see that sound propagation can be isolated from heat diffusion whenever k is so small that

$$(D_T k^2)^2 \ll c^2 k^2.$$

For these wavelengths the solutions to (54), omitting only terms of order $(D_T k/c)^2$, are

$$\begin{aligned} n(\mathbf{k}, z) = {} & p(\mathbf{k}) \left.\frac{\partial n}{\partial p}\right|_T \left(1 - \frac{c_v}{c_p}\right) [-iz + D_T k^2]^{-1} \\ & - p(\mathbf{k}) \left.\frac{\partial n}{\partial p}\right|_T \left[\Gamma \frac{c_v}{c_p} k^2 + D_T \left(1 - \frac{c_v}{c_p}\right) k^2 - iz \frac{c_v}{c_p}\right] [z^2 - c^2 k^2 + iz\Gamma k^2]^{-1} \\ & + T(\mathbf{k}) \left.\frac{\partial n}{\partial T}\right|_p [-iz + D_T k^2]^{-1} - T(\mathbf{k}) \left.\frac{\partial n}{\partial T}\right|_p D_T k^2 [z^2 - c^2 k^2 + iz\Gamma k^2]^{-1} \end{aligned} \tag{56}$$

and

$$\begin{aligned} q(\mathbf{k}, z) = {} & T(\mathbf{k})\, mnc_p [-iz + D_T k^2]^{-1} + p(\mathbf{k}) \frac{T}{V} \left.\frac{\partial S}{\partial p}\right|_T [-iz + D_T k^2]^{-1} \\ & - p(\mathbf{k}) \frac{T}{V} \left.\frac{\partial S}{\partial p}\right|_T D_T k^2 [z^2 - c^2 k^2 + iz\Gamma k^2]^{-1}, \end{aligned} \tag{57}$$

where c_v and c_p are the specific heats at constant volume and pressure

$$mnc_p = \frac{T}{V} \left.\frac{\partial S}{\partial T}\right|_p$$

$$mnc_v = \frac{T}{V} \left.\frac{\partial S}{\partial T}\right|_n .$$

In this more general situation, the sound velocity is given by

$$mc^2 = \left.\frac{\partial p}{\partial n}\right|_S = \frac{c_p}{c_v} \left.\frac{\partial p}{\partial n}\right|_T \tag{58}$$

while the thermal diffusivity and the sound wave damping constants are

$$D_T = \kappa / mnc_p \tag{59}$$

$$\Gamma = D_l + D_T([c_p/c_v) - 1]. \tag{60}$$

B. *Construction of Disturbance for Correlation Function Description*

Before we can use the solution for the hydrodynamic equations that we have just derived, we must look into the following conceptual problem. We wish to compare the previous description with a description in which we mechanically displace a system from equilibrium in such a way that all variations in time and space are slow. In our discussion of spin diffusion there was a very natural mechanism by which this deviation from complete equilibrium could be mechanically induced. The spin magnetic moment could be altered by applying an external magnetic field. There exists no such handle for the molecules in a fluid. In particular, the mechanical forces by which a heat conduction process is set up are rather subtle.

Now almost any force which disturbs the system from equilibrium will set up heat conduction and sound propagation processes, and if we wait long enough, these will be the only modes we will generally find. However if we are to infer the form of the correlation functions from the hydrodynamic equations, which are only true when the system is in local equilibrium, we must apply a disturbance which guarantees that the system is in local equilibrium at all times, not just for long times. That is to say, we must select an interaction Hamiltonian which disturbs the system in such a way that the system is even in local equilibrium initially.

To aid us in choosing such a mechanical disturbance, we recall the method for computing the average value of an operator, $A(\mathbf{r}, t)$, in a system in full equilibrium. If the system is moving with a velocity $\mathbf{v}$, the average of A in the grand canonical ensemble is

$$\begin{aligned}\langle A(\mathbf{r}, t)\rangle &= \mathrm{tr}[\rho A(\mathbf{r}, t)]\\ \rho &= \exp \Xi[\mathrm{Tr} \exp \Xi]^{-1}\\ \Xi &= -\beta\left[\mathscr{H}_0 - \mu\mathfrak{N} + \tfrac{1}{2}mv^2\mathfrak{N} - \int d\mathbf{r}\mathbf{g}(\mathbf{r})\cdot\mathbf{v}\right].\end{aligned} \tag{61}$$

The thermodynamic state of the system is described by μ, β, and $\mathbf{v}$. If the velocity is small, the v^2 term in (61) may be neglected.

We note that it is possible to represent a situation in which the chemical potential changes from μ to $\mu+\delta\mu$, the temperature changes from T to $T+\delta T$, and the velocity goes from zero to $\delta\mathbf{v}$ by writing the density matrix in the complete equilibrium form

$$\rho = \exp[-\beta(\mathscr{H} - \mu\mathfrak{N})]\{\mathrm{Tr} \exp[-\beta(\mathscr{H} - \mu\mathfrak{N})]\}^{-1}$$

with a modified Hamiltonian, $\mathscr{H}_0 + \delta\mathscr{H}$, where

$$\delta\mathscr{H} = -\int d\mathbf{r}\left\{\frac{\delta T}{T}[\epsilon(\mathbf{r}) - \mu n(\mathbf{r})] + \delta\mu n(\mathbf{r}) + \delta\mathbf{v}\cdot g(\mathbf{r})\right\}. \tag{62}$$

In analogy with (62) it is appealing to use the interaction Hamiltonian

$$\begin{aligned}\delta\mathscr{H}(t) &= -\int d\mathbf{r}\left\{\frac{\delta T(\mathbf{r})}{T}\left[\epsilon(\mathbf{r},t)-\mu n(\mathbf{r},t)\right]+\delta\mu(r)\,n(\mathbf{r},t)+\delta\mathbf{v}(r)\cdot\mathbf{g}(\mathbf{r},t)\right\}e^{\varepsilon t}\\ &\qquad \text{for}\quad t<0,\\ &=0 \qquad \text{for}\quad t>0\end{aligned} \tag{63}$$

to represent a situation in which the system is in local thermodynamic equilibrium for all times less than zero. We would, of course, guess that the local velocity would be $\delta\mathbf{v}(\mathbf{r})$, the local temperature $T+\delta T(\mathbf{r})$ and the local chemical potential $\mu+\delta\mu(\mathbf{r})$. If we can show that the system is in local thermodynamic equilibrium for times less than zero, then we can use (63) as an interaction Hamiltonian for producing hydrodynamic flow.

To justify the use of (63), we must prove that for all times less than zero, the average of any operator $A(r,t)$ changes from its complete equilibrium value by the amount

$$\delta\langle A(\mathbf{r},t)\rangle=\left.\frac{\partial A}{\partial\mu}\right|_{T,\mathbf{v}}\delta\mu(\mathbf{r})+\left.\frac{\partial A}{\partial T}\right|_{\mu,\mathbf{v}}\delta T(\mathbf{r})+\left.\frac{\partial A}{\partial\mathbf{v}}\right|_{\mu,T}\cdot\delta\mathbf{v}(\mathbf{r})\qquad\text{for}\quad t<0. \tag{64}$$

The derivatives indicated in (64) are, of course, thermodynamic derivatives.

The proof of (64) is essentially identical with the proof (in Section II, C) that $\lim_{k\to0}\chi(k)$ is the thermodynamic derivative dM/dH. For simplicity, we consider the case in which $\delta\beta=\delta\mathbf{v}=0$. We write a spectral form for the $A-n$ commutator

$$\langle[A(\mathbf{r},t),n(\mathbf{r}',t')]\rangle=\int\frac{d\omega}{\pi}\int\frac{d\mathbf{k}}{(2\pi)^3}e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')-i\omega(t-t')}\chi''_{A,n}(\mathbf{k},\omega).$$

According to the fluctuation–dissipation theorem (Eq. (43)) the $A-n$ anticommutator is

$$\begin{aligned}&\langle\{A(\mathbf{r},t)-\langle A\rangle_{\text{eq.}},n(\mathbf{r}',t')-\langle n\rangle_{\text{eq.}}\}\rangle_{\text{eq.}}\\ &\quad=\int\frac{d\omega}{\pi}\int\frac{d\mathbf{k}}{(2\pi)^3}e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')-i\omega(t-t')}\chi''_{An}(\mathbf{k},\omega)\coth\frac{\beta\omega}{2}.\end{aligned}$$

We can calculate the thermodynamic derivative $\partial A/\partial\mu$ from Eq. (61), obtaining

$$\left.\frac{\partial A}{\partial\mu}\right|_{T,\mathbf{v}}=\frac{\beta}{2}\int d\mathbf{r}'[\langle\{A(\mathbf{r},t),n(\mathbf{r}',t')\}\rangle_{\text{eq.}}-\langle A\rangle_{\text{eq.}}\langle n\rangle_{\text{eq.}}].$$

It is of course implicit in writing this equation that the static correlation function has no long range part or that the integral converges. This is not the case with

$\partial A/\partial v$ or $\{A, v\}$ in a superfluid. Apart from such exceptional situations, we may write

$$\left.\frac{\partial A}{\partial \mu}\right|_{T,v} = \int \frac{d\omega}{\pi}\frac{\beta}{2}\coth\frac{\beta\omega}{2}\chi''_{A,n}(\mathbf{0},\omega).$$

Since the total number of particles is independent of time $\chi''_{A,n}(0,\omega)/\omega$ must be just a delta function at zero frequency. Therefore, just as before, we can make the replacement

$$(\beta\omega/2)\coth(\beta\omega/2)\,\chi''_{An}(\mathbf{0},\omega) = \chi''_{An}(\mathbf{0},\omega)$$

and find

$$\left.\frac{\partial A}{\partial \mu}\right|_{T,v} = \int \frac{d\omega}{\pi}\frac{\chi''_{An}(\mathbf{0},\omega)}{\omega}. \tag{65}$$

We can use Eq. (12) to calculate the response to the time-dependent disturbance (63). Then, in just the same way as we obtained Eq. (15), we find

$$\delta\langle A(\mathbf{r},t)\rangle = \int \frac{d\mathbf{k}}{(2\pi)^3}\mu(\mathbf{k})\,e^{i\mathbf{k}\cdot\mathbf{r}}\int\frac{d\omega}{\pi}\frac{\chi''_{An}(\mathbf{k},\omega)}{\omega} \qquad \text{for} \quad t \leqq 0,$$

where $\mu(\mathbf{k})$ is the Fourier transform of $\delta\mu(\mathbf{r})$. Thus $A(\mathbf{k})$, the Fourier transform of $\delta\langle A(\mathbf{r},0)\rangle$, is

$$A(\mathbf{k}) = \mu(\mathbf{k})\int\frac{d\omega}{\pi}\frac{\chi''_{An}(\mathbf{k},\omega)}{\omega}. \tag{66}$$

If $\delta\mu(\mathbf{r})$ contains only very small wave numbers (or equivalently, varies slowly in space) then the $\mathbf{k}$ which appears in (66) may be replaced by $\mathbf{0}$. A comparison of (65) and (66) indicates that

$$A(\mathbf{k}) = \left.\frac{\partial A}{\partial \mu}\right|_{T,\mathbf{v}}\mu(\mathbf{k})$$

or

$$\delta\langle A(\mathbf{r},t)\rangle = \left.\frac{\partial A}{\partial \mu}\right|_{T,\mathbf{v}}\delta\mu(\mathbf{r}) \qquad \text{for} \quad t<0.$$

In this way we can verify that Eq. (64) is valid whenever $\delta\mu(\mathbf{r})$, $\delta T(\mathbf{r})$, and $\delta\mathbf{v}(\mathbf{r})$ vary sufficiently slowly in space. In the limit of slow variation, the system appears to be in local thermodynamic equilibrium and $\mu+\delta\mu(\mathbf{r})$, $T+\delta T(\mathbf{r})$, $\delta\mathbf{v}(\mathbf{r})$ are just the local chemical potential, temperature, and velocity.

This is, however, a weak link in this derivation of (64), namely, our assumption that

$$\lim_{\mathbf{k}\to 0}\int \frac{d\omega}{\pi}\frac{\chi''_{ij}(\mathbf{k},\omega)}{\omega}=\int\frac{d\omega}{\pi}\frac{\chi''_{ij}(\mathbf{0},\omega)}{\omega}.$$

There are situations in which $\mathbf{k}=\mathbf{0}$ is quite different from all $\mathbf{k}\neq\mathbf{0}$. This difference will appear whenever there are infinitely long-ranged correlations. These correlations tend to affect $\mathbf{k}=\mathbf{0}$ modes very differently from $\mathbf{k}\neq\mathbf{0}$ ones. Thus, for example, in a Coulomb system, the exact shape and nature of the surface will determine the behavior of the plasma oscillation at $\mathbf{k}=\mathbf{0}$. Also, in a superfluid, the surfaces and past history of the body will determine the relative proportions of superfluid and normal flow at $\mathbf{k}=\mathbf{0}$. This effect appears because of the infinitely long-ranged correlations in the superfluid component. Thus, in these cases, Eq. (64) fails to be correct.

For the purposes of the above argument, the chemical potential, the temperature, and the velocity were a convenient complete set of variables. However, the chemical potential does not have any direct physical meaning in the one-component system. Consequently, it is more convenient to eliminate the local chemical potential in favor of the local pressure by using the thermodynamic relation

$$dp=n\,d\mu+(S/V)\,dT=n\,d\mu+(\epsilon+p-\mu n)\,dT/T \tag{67a}$$

to define

$$p(\mathbf{k})=n\mu(\mathbf{k})+(\epsilon+p-\mu n)\,T(\mathbf{k})/T. \tag{67b}$$

To see that $p(\mathbf{k})$ has the significance of a change in the pressure in the limit of slow spatial variation, it is only necessary to use the thermodynamic relation (67a) to rewrite (64) as

$$\begin{aligned}A(\mathbf{r},t)=&\left[n\delta\mu(\mathbf{r})+(\epsilon+p-\mu n)\frac{\delta T(\mathbf{r})}{T}\right]\frac{\delta A}{\delta p}\bigg|_{T,\mathbf{v}}\\&+\delta T(\mathbf{r})\frac{\delta A}{\delta T}\bigg|_{p,\mathbf{v}}+\mathbf{v}(\mathbf{r})\cdot\frac{\partial A}{\partial\mathbf{v}}\bigg|_{p,T}.\end{aligned}$$

Then, if we use (67b) to define

$$\begin{aligned}\delta p(\mathbf{r})&=n\delta\mu(\mathbf{r})+(\epsilon+p-\mu n)\,\delta T(\mathbf{r})/T\\&\equiv\int\frac{d\mathbf{k}}{(2\pi)^3}\,e^{i\mathbf{k}\cdot\mathbf{r}}p(\mathbf{k}),\end{aligned}$$

we have

$$\delta\langle A(\mathbf{r},t)\rangle = \delta p(\mathbf{r}) \left.\frac{\delta A}{\delta p}\right|_{T,\mathbf{v}} + \delta T(\mathbf{r}) \left.\frac{\delta A}{\delta T}\right|_{p,\mathbf{v}} + \delta\mathbf{v}(\mathbf{r}) \cdot \left.\frac{\partial A}{\partial \mathbf{v}}\right|_{T,p} \tag{68}$$

so that $\delta p(\mathbf{r})$ does indeed have the meaning of a change in the pressure.

Finally, we eliminate $\delta\mu(\mathbf{r})$ from the disturbance (63) by making use of (67b). With this substitution Eq. (63) becomes

$$\begin{aligned} \delta\mathscr{H}(t) &= -\int d\mathbf{r} \left[\frac{\delta p(\mathbf{r})}{\langle n\rangle} n(\mathbf{r},t) + \frac{\delta T(\mathbf{r})}{T} q(\mathbf{r},t) + \mathbf{v}(\mathbf{r}) \cdot \mathbf{g}(\mathbf{r},t) \right] e^{\epsilon t} \qquad \text{for} \quad t<0, \\ &= 0 \qquad \text{for} \quad t>0, \end{aligned} \tag{69}$$

where $q(\mathbf{r},t)$ is the operator previously encountered which represents changes in the density of heat energy

$$q(\mathbf{r},t) = \epsilon(\mathbf{r},t) - \frac{\langle\epsilon\rangle + p}{\langle n\rangle} n(\mathbf{r},t).$$

C. *Representation of the Commutators*

We can now write the response of the system to the disturbance (69) as

$$\begin{aligned} \delta\langle A(\mathbf{r},t)\rangle &= \int_{-\infty}^{t} dt' \int d\mathbf{r}' e^{\epsilon t'} \{\ \} \qquad \text{for} \quad t<0, \\ &= \int_{-\infty}^{0} dt' \int d\mathbf{r} e^{\epsilon t'} \{\ \} \qquad \text{for} \quad t>0, \end{aligned}$$

where

$$\begin{aligned} \{\ \} = {} & \langle [A(\mathbf{r},t), n(\mathbf{r}',t')] \rangle_{\text{eq.}} \delta p(\mathbf{r}')/n + \langle [A(\mathbf{r},t), q(\mathbf{r}',t')] \rangle_{\text{eq.}} \delta T(\mathbf{r}')/T \\ & + \langle [A(\mathbf{r},t), \mathbf{g}(\mathbf{r}',t')] \rangle_{\text{eq.}} \cdot \mathbf{v}(\mathbf{r}'). \end{aligned}$$

We introduce the representation (42a) for the commutators, the A_i being q, n, and the components of $\mathbf{g}$. For times less than zero, we then have

$$\begin{aligned} A(\mathbf{k}) = {} & \int \delta\langle A(\mathbf{r},t)\rangle \, e^{-i\mathbf{k}\cdot\mathbf{r}} \, d\mathbf{r} \\ & + \int \frac{d\omega}{\pi} \frac{\chi''_{A,n}(\mathbf{k},\omega)}{\omega} \frac{p(\mathbf{k})}{n} + \int \frac{d\omega}{\pi} \frac{\chi''_{A,q}(\mathbf{k},\omega)}{\omega} \frac{T(\mathbf{k})}{T} \\ & + \int \frac{d\omega}{\pi} \frac{\chi''_{A,\mathbf{g}}(\mathbf{k},\omega)}{\omega} \cdot \mathbf{v}(\mathbf{k}). \end{aligned} \tag{70}$$

For times greater than zero, the response may be represented by

$$A(\mathbf{k}, z) = \int_0^\infty dt e^{izt} \int d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}}\, \delta\langle A(\mathbf{r}, t)\rangle$$

$$= \int \frac{d\omega}{\pi i} \frac{\chi''_{A,n}(\mathbf{k}, \omega)}{\omega(\omega - z)} \frac{p(\mathbf{k})}{n} + \int \frac{d\omega}{\pi i} \frac{\chi''_{A,q}(\mathbf{k}, \omega)}{\omega(\omega - z)} \frac{T(\mathbf{k})}{T}$$

$$+ \int \frac{d\pi}{\pi i} \frac{\chi''_{A,\mathbf{g}}(\mathbf{k}, \omega)}{\omega(\omega - z)} \cdot \mathbf{v}(\mathbf{k}). \tag{71}$$

We are interested in the cases in which $A(\mathbf{r}, t)$ is $n(\mathbf{r}, t)$, $q(\mathbf{r}, t)$, or $\mathbf{g}(\mathbf{r}, t)$. Therefore, we shall briefly discuss the properties of the Fourier transforms of the commutators formed from these conserved operators. By using time-reversal invariance, rotational invariance, and the Hermitian nature of the operators, one can show that $\chi''_{n,n}$, $\chi''_{q,q}$, $\chi''_{n,q}$ and $\chi''_{q,n}$ are each real odd functions of ω, and that

$$\chi''_{n,q}(k, \omega) = \chi''_{q,n}(k, \omega). \tag{72}$$

Equation (72) expresses a reciprocity which was first discussed by Onsager [16]. From (71) and (72) it follows that the response of the density to a change in the temperature (at constant pressure) differs by only a factor of n from the change in the entropy density induced by a change in the pressure (at constant temperature). In more complex situations than those we shall consider here, this reciprocity leads to a connection between transport coefficients which would otherwise have no obvious relation with one another.

The Fourier transform of the momentum–momentum commutator is a tensor, since it is an average of a direct product of two vectors. However, the only tensor quantities of which $\chi''_{g_i, g_j}(\mathbf{k}, \omega)$ could be composed, in the absence of long-range correlations, are the direct product $k_i k_j$ and the unit matrix $\delta_{i,j}$. We find it convenient to express χ''_{g_i, g_j} in terms of linear combinations of these as

$$\chi''_{g_i, g_j} = (k_i k_j / k^2)\, \chi''_l(k, \omega) + (\delta_{ij} - k_i k_j / k^2)\, \chi''_t(k, \omega). \tag{73}$$

Here the l and t stand for longitudinal and transverse since the splitting that we have indicated in (73) divides the tensor into two parts, one with components in the direction of k, the other whose dot product with k is zero. Both parts are real functions, odd in the frequency variable.

The conservation law

$$\frac{\partial n}{\partial t} + \frac{1}{m} \nabla \cdot \mathbf{g} = 0$$

enables us to express $\chi''_{\mathbf{g},n}$ in terms of χ''_l as

$$\chi''_{n,\mathbf{g}}(\mathbf{k}, \omega) = \chi''_{\mathbf{g},n}(\mathbf{k}, \omega) = \frac{\mathbf{k}}{m\omega} \chi''_l(k, \omega) \tag{74}$$

while a double application of this law gives

$$\chi''_{n,n}(k,\omega)=\frac{k^2}{m^2\omega^2}\chi''_l(k,\omega). \tag{75}$$

One more result of the number conservation law is

$$\chi''_{\mathbf{g},q}(\mathbf{k},\omega)=\chi''_{q,\mathbf{g}}(\mathbf{k},\omega)=\frac{\mathbf{k}}{m\omega}\chi''_{q,n}(k,\omega). \tag{76}$$

D. *Sum Rules*

By comparing Eqs. (70) and (68) we can deduce a variety of Kramers–Kronig relation sum rules analogous to Eq. (26) for the integrals of the various commutators. For example, we may take $A(\mathbf{r},t)=n(\mathbf{r},t)$. Then Eq. (68) gives

$$n(\mathbf{k})=\left.\frac{\partial n}{\partial p}\right|_T p(\mathbf{k})+\left.\frac{\partial n}{\partial T}\right|_p T(\mathbf{k})$$

so that Eq. (70) implies

$$\lim_{k\to 0}\int\frac{d\omega}{\pi}\frac{\chi''_{n,n}(k,\omega)}{\omega}=\lim_{k\to 0}\chi_{nn}(k)=n\left.\frac{\partial n}{\partial p}\right|_T \tag{77a}$$

$$\lim_{k\to 0}\int\frac{d\omega}{\pi}\frac{\chi''_{n,q}(k,\omega)}{\omega}=T\left.\frac{\partial n}{\partial T}\right|_p. \tag{77b}$$

For $A(\mathbf{r},t)=q(\mathbf{r},t)$ we find

$$\lim_{k\to 0}\int\frac{d\omega}{\pi}\frac{\chi''_{n,q}(k,\omega)}{\omega}=n\frac{T}{V}\left.\frac{\partial S}{\partial p}\right|_T=T\left.\frac{\partial n}{\partial T}\right|_p \tag{77c}$$

$$\lim_{k\to 0}\int\frac{d\omega}{\pi}\frac{\chi''_{q,q}(k,\omega)}{\omega}=\frac{T^2}{V}\left.\frac{\partial S}{\partial T}\right|_p=mnc_pT. \tag{77d}$$

For $A(\mathbf{r},t)=\mathbf{g}(\mathbf{r},t)$

$$A(\mathbf{k})=mn\,\mathbf{v}(\mathbf{k})$$

so that Eq. (70) implies

$$\lim_{k\to 0}\int\frac{d\omega}{\pi}\frac{\chi''_{g_ig_j}(k,\omega)}{\omega}=\delta_{ij}mn$$

which may be written

$$\lim_{k\to 0}\int \frac{d\omega}{\pi}\frac{\chi''_{\mathrm{t}}(k,\omega)}{\omega}=mn \tag{77e}$$

and

$$\int \frac{d\omega}{\pi}\frac{\chi''_{l}(k,\omega)}{\omega}=\int \frac{d\omega}{\pi}\frac{\omega^2 m^2}{k^2}\frac{\chi''_{nn}(k,\omega)}{\omega}=mn. \tag{77f}$$

Finally, by using the fact that the heat current is zero even when the system is in motion, it is possible to show that

$$\lim_{k\to 0}\int \frac{d\omega}{\pi}\chi_{j^q,\,g}(k,\omega)=0.$$

By using the conservation laws, we can derive from this relation the sum rule

$$\lim_{k\to 0}\int \frac{d\omega}{\pi}\frac{\omega^2}{mk^2}\chi''_{q,\,n}(k,\omega)=0. \tag{77g}$$

Since Eq. (68) is only valid for small k, the sum rules (77) need only be valid in this limit. However, not all of the identities are really subject to this restriction. Equation (77f), which expresses a sum rule on the density–density correlation function is, in fact, valid for all k. This sum rule can be derived from an argument identical to the one that we used to get (27). That is to say, this result is a consequence of the exact commutation relation

$$[n(\mathbf{r}),\mathbf{g}(\mathbf{r}')]=-i\nabla[n(\mathbf{r})\,\delta(\mathbf{r}-\mathbf{r}')]$$

which holds whenever there are velocity-independent forces. In fact, the sum rule (77f) is a famous result. In solid state physics, it is usually referred to as the longitudinal f-sum rule. It has played a very important role in the discussion of the BCS theory of superconductivity.[11] In neutron scattering studies, it is known as the Placzek sum rule [9].

In the classical limit, subject to the existence of the velocity correlation function Fourier transform or the absence of long-range order, (77e) is also exact for all k. It is a statement of the van Leeuwen theorem that the orbital magnetic susceptibility of a classical system vanishes. Landau [18] has discussed how diamagnetic susceptibility can, in fact, appear in a quantum mechanical system. In our language, this is a consequence of the fact that

$$\chi_l(k)-\chi_{\mathrm{t}}(k)=\mathcal{O}(k^2)$$

can contain a term of order k^2 in the limit of small k^2.

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[11] See, for example, Ref. [17].

The quantum effects are even more drastic in a superfluid. In a superfluid (77e) is not even satisfied in the limit $k^2 \to 0$. This failure of the sum rule is reflected in the anomalous electromagnetic properties of the superconductor, the Meissner effect and the persistence of supercurrents and in the corresponding properties of liquid helium. The source of this failure has been indicated. In superfluids, correlation functions which involve the momentum die off too slowly in space to permit the analysis we have employed.

The sum rule (77a) is particularly interesting since it is an additional sum rule on the density–density correlation function, a function which is very important both experimentally and theoretically.[12]

An alternative, and very useful, expression of these sum rules is given by taking the limit as z goes to infinity in Eq. (71). Then if A is n, q, and $\mathbf{g}$, we find

$$\lim_{z \to \infty} -izn(\mathbf{k}, z) = p(\mathbf{k}) \left[\left.\frac{\partial n}{\partial p}\right|_T + \frac{k^2}{mz^2} + \mathcal{O}\left(\frac{1}{z^3}\right) \right] + T(\mathbf{k}) \left[\left.\frac{\partial n}{\partial T}\right|_p + \mathcal{O}\left(\frac{1}{z^3}\right) \right] + \mathbf{k} \cdot \mathbf{v}(\mathbf{k}) \left[\frac{1}{z} + \mathcal{O}\left(\frac{1}{z^2}\right) \right] \tag{78a}$$

$$\lim_{z \to \infty} -izq(\mathbf{k}, z) = p(\mathbf{k}) \left[\left.\frac{T}{V}\frac{\partial S}{\partial p}\right|_T + \mathcal{O}\left(\frac{1}{z^3}\right) \right] + T(\mathbf{k}) \left[mnc_p + \mathcal{O}\left(\frac{1}{z}\right) \right] + \mathbf{k} \cdot \mathbf{v}(\mathbf{k})\, \mathcal{O}\left(\frac{1}{z^2}\right) \tag{78b}$$

$$\lim_{z \to \infty} -iz\mathbf{g}(\mathbf{k}, z) = \mathbf{v}(\mathbf{k})[mn + \mathcal{O}(1/z)] + \mathbf{k}p(\mathbf{k})[1 + \mathcal{O}(1/z)] + \mathbf{k}T(\mathbf{k})\, \mathcal{O}(1/z). \tag{78c}$$

Notice that these expressions agree, as they must, with the results of our hydrodynamic analysis as given in Eqs. (51), (56), and (57).

E. *Low Temperature Forms for Correlation Functions*

The hydrodynamic analysis led to particularly simple forms for the correlation functions in the low temperature limit. (See Eqs. (55a) and (55b).) The response $q(\mathbf{k}, z)$ had no term proportional to $p(\mathbf{k})$ and was proportional to $T(\mathbf{k})$. By comparing (55b) and (71), we see that for z in the upper half of the complex plane

$$\int \frac{d\omega'}{\pi i} \frac{\chi''_{q,q}(k, \omega')}{\omega'(\omega' - z)} = \frac{T^2}{V} \frac{dS}{dT} \left[-iz + \kappa k^2 \frac{V}{T} \frac{dT}{dS} \right]^{-1}. \tag{79}$$

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[12] This sum rule, of course, expresses information about both the commutator and the anticommutator of the density. In its anticommutator form, this result was used by Ornstein and Zernicke in their classical work on critical fluctuations. It has been more recently employed by Ziman [19a]. The commutator form has been known to the authors for quite some time. It was discussed by Mermin [19b]. It has more recently been stressed by Pines.

Since

$$\chi''_{q,q}(k,\omega)=\mathrm{Re}\int\frac{d\omega'}{\pi i}\frac{\chi''_{q,q}(k,\omega')}{\omega'(\omega'-\omega-i\epsilon)}$$

we find the same diffusion structure for this heat-energy correlation function as we found for the spin density correlation function, namely,

$$\chi''_{qq}(k,\omega)-\kappa Tk^2\omega\left[\omega^2+\left(\kappa k^2\frac{V}{T}\frac{dT}{dS}\right)^2\right]^{-1}. \tag{80}$$

(See, for comparison, Eq. (19).)

In the low temperature case, the response of the density is also simple since it contains, according to (55a), no term proportional to $T(k)$ but only a term proportional to $p(k)$. By comparing (55a) and (71) we see

$$\int\frac{d\omega}{\pi i}\frac{\chi''_{n\,n}(k,\omega)}{\omega(\omega-z)}=-\frac{1}{iz}n\frac{\partial n}{\partial p}\left[1+\frac{1}{m}\frac{\partial p}{\partial n}k^2\left(z^2-\frac{1}{m}\frac{\partial p}{\partial n}k^2+iD_l zk^2\right)^{-1}\right] \tag{81}$$

and consequently

$$\chi''_{n,n}(k,\omega)=\frac{nk^4\Gamma\omega}{m}\left[\left(\omega^2-\frac{1}{m}\frac{dp}{dn}k^2\right)^2+(\Gamma\omega k^2)^2\right], \tag{82}$$

where $\Gamma=D_l$.

Equations (81) and (82) give the density response in the limit of small k. But, because the density correlation function is such an important quantity both experimentally and theoretically, it is worthwhile for us to examine some of the general properties of this function. Our analysis in this case closely parallels the establishment of a dispersion relation for $M(\mathbf{k},z)$ in section E of the chapter on spin response. In analogy with this work we define

$$\chi_{n,n}(k,z)=\int\frac{d\omega}{\pi}\frac{1}{\omega-z}\chi''_{n,n}(k,\omega)$$

and

$$\chi_{n,n}(k)=\chi_{n,n}(k,0) \tag{83}$$

and notice that the facts

$$\lim_{z\to\infty}\chi_{n,n}(k,z)=-\frac{1}{z^2}\int\frac{d\omega}{\pi}\omega\chi''_{n,n}(k,\omega)=-\frac{k^2n}{mz^2}$$

$$\omega\chi''_{n,n}(k,\omega)\geqq 0$$

imply the dispersion relation

$$\frac{1}{z^2}\left[\frac{\chi_{n,n}(k)}{\chi_{n,n}(k,z)}-1\right]=-\frac{m\chi_{n,n}(k)}{nk^2}-\int\frac{d\omega'}{\pi}\frac{f_{n,n}(k,\omega')}{\omega' z(\omega'-z)}.$$

When z lies just above the real axis, we have

$$\frac{\chi_{M,M}(k)}{\chi_{M,M}(k,\omega+i\epsilon)}-1=-\frac{m\omega^2}{nk^2}\chi_{n,n}(k)-if_{n,n}(k,\omega)+\mathscr{P}\int\frac{d\omega'}{\pi}\frac{\omega}{\omega'}\frac{f_{n,n}(k,\omega')}{(\omega-\omega')}. \tag{84}$$

This result should be compared with Eq. (38) which gave the spin response as

$$\frac{\chi_{M,M}(k)}{\chi_{M,M}(k,\omega+i\epsilon)}-1=-\frac{4m\omega^2\chi(k)}{nk^2\gamma^2}-if_{M,M}(k,\omega)+\mathscr{P}\int\frac{d\omega'}{\pi}\frac{\omega}{\omega'}\frac{f_{M,M}(k,\omega')}{(\omega-\omega')}. \tag{38}$$

In the spin case, $f(k,\omega)$ reduced to ω/k^2D_M in the limit as the wave number and the frequency went to zero. Therefore, we decided to define a frequency- and wave number-dependent diffusivity by

$$f_{M,M}(k,\omega)=\omega/k^2D_M(k,\omega). \tag{39}$$

In this sound wave propagation situation, Eq. (81) implies that for small k^2,

$$\frac{1}{\chi_{n,n}(k,\omega+i\epsilon)}-\frac{1}{\chi_{n,n}(k)}=\frac{1}{\chi_{n,n}(k,\omega+i\epsilon)}-\frac{1}{n}\frac{dp}{dn}=-\frac{m\omega^2}{nk^2}-i\omega\Gamma\frac{m}{n}.$$

Therefore, we can write the spectral weight function which appears in (84) as

$$f_{n,n}(k,\omega)=\chi_{n,n}(k)\,\Gamma(k,\omega)\frac{m}{n}\omega$$

with the knowledge that for low temperature systems $\Gamma(k,\omega)$ reduces to the sound wave damping constant, $\Gamma=D_l$, in the limit as the frequency and wave number go to zero. With this definition the spectral function of (84) becomes

$$\chi_{n,n}^{-1}(k,\omega+i\epsilon)-\chi_{n,n}^{-1}(k)=-\frac{m\omega^2}{nk^2}-\frac{m}{n}i\omega\Gamma(k,\omega)+\frac{m\omega}{n}\mathscr{P}\int\frac{d\omega'}{\pi}\frac{\Gamma(k,\omega')}{\omega-\omega'}. \tag{85}$$

Consequently, an exact form for $n(k, z)/p(k)$ is

$$\left.\frac{n(k,z)}{p(k)}\right|_{z=\omega+i\epsilon} = -\frac{1}{\omega}\left\{\chi_{n,n}(k) - \left[\chi^{-1}_{n,n}(k) - \frac{m\omega^2}{nk^2} - i\omega\Gamma(k,\omega)\frac{m}{n} + \frac{m\omega}{n}\mathscr{P}\int\frac{d\omega'}{\pi}\frac{\Gamma(k,\omega')}{\omega-\omega'}\right]^{-1}\right\}$$

and

$$\chi''_{n,n}(k,\omega) = \frac{\dfrac{n}{m}\Gamma(k,\omega)\,k^4\omega}{\left(\omega^2 - \dfrac{n}{m}\dfrac{k^2}{\chi^{-1}_{n,n}(k)} - \omega^2k^2\mathscr{P}\displaystyle\int\frac{d\omega'}{\pi}\frac{\Gamma(k,\omega)}{\omega^2-\omega'^2}\right)^2 + [\omega k^2\Gamma(k,\omega)]^2}. \quad (86)$$

We should emphasize that the equations (85) and (86) are exact. However, whether or not these equations are useful depends critically upon the simplicity, or lack thereof, of the function $\Gamma(k, \omega)$. In the particular case of a low temperature ordinary fluid, we have seen that the equations of fluid mechanics imply that $\Gamma(k, \omega)$ goes to the constant Γ for low frequencies and small wave numbers with $\omega \sim ck$ and also that $\chi_{n,n}(k) \to n(dp/dn)^{-1}$. However, at nonvanishing temperature $\Gamma(k, \omega)$ depends on the manner in which ω and k approach zero, since $\chi''_{n,n}(k, \omega)$ must include the thermal diffusion process indicated in (56). That is to say, Γ, like χ'', has different limits, depending on the ratio of ω and k as they both approach zero. Specifically it can be shown that $f(k, \omega)$ has a term which behaves like

$$f \cong \left(\frac{c_p}{c_v} - 1\right) D_T k^2 \omega \left[\omega^2 + D_T{}^2\left(\frac{c_p}{c_v}\right)^2 k^4\right]^{-1}$$

for small k and ω.

We next comment further on the significance of the function $f(k, \omega)$. We observe that the part to which we have just referred has poles at $\omega = \pm i D_T(c_p/c_v)\,k^2 = \pm i(\kappa/mn)\,k^2$ corresponding to relaxation as a result of thermal conduction. In addition, the function $f(k, \omega)$ contained the term which at low frequencies became $m\omega\Gamma\chi/n$. This term vanished at high frequencies. Both terms are consistent with a form

$$f(k,\omega) = \int_0^\infty \frac{d\tau}{\tau}\frac{\phi(k,\tau)}{\omega^2+(1/\tau)^2}\frac{\omega m\chi}{n} \qquad \text{or} \qquad \sum_i \frac{\phi_i(k)\,\omega}{\tau_i(k)(\omega^2+(1/\tau_i(k))^2}\frac{m\chi}{n}.$$

Conversely, such a form would give rise to an expression for $\chi^{-1}(k, z)$

$$\chi^{-1}(k,z) = -\frac{m}{n}\frac{z^2}{k^2} + \chi^{-1}(k) + \chi^{-1}(k)\,z\mathscr{P}\int\frac{d\omega'}{\pi}\frac{f(k,\omega')}{\omega'(z-\omega')}$$

which could be rewritten for z in the upper half-plane as

$$= -\frac{m}{n}\left\{\frac{z^2}{k^2} - c_\infty{}^2 - \int_0^\infty d\tau\, \frac{1}{1 - iz\tau}\,\phi(k, \tau)\right\}$$

or

$$= -\frac{m}{n}\left\{\frac{z^2}{k^2} - c_\infty{}^2 - \sum_i \frac{\phi_i(k)}{1 - iz\tau_i(k)}\right\},$$

where

$$c_\infty{}^2 \equiv \frac{n}{m\chi} + \int_0^\infty d\tau \phi(k, \tau), \qquad \text{or} \qquad \frac{n}{m\chi} + \sum_i \phi_i(k).$$

The form we have hypothesized therefore corresponds to a weighted distribution of relaxation times, τ. Experimental evidence [20] seems to indicate that at least this complicated a form is required. Such a form would be obtained if the function $f(k, \omega)$ could be calculated and if its analytic continuation into the lower half ω-plane only possessed poles or a branch line on the negative imaginary axis. Generally, however, there may be both real and imaginary parts to the singularities of f, and therefore of continuations of $\chi^{-1}(k, z)$ into the lower half plane. Under these circumstances f contains a distribution of resonant frequencies as well as a distribution of relaxation times.

Finally we remark without exhibiting details that the phase representation, which is convenient for carrying out stationary phase asymptotic evaluations of $\chi^{-1}(k, z)$, in the general case reduces to

$$\omega \cot\ \delta(k, \omega) \cong \frac{c_v}{c_p}\, \frac{(\omega^2 - c^2k^2)\,\omega^2}{Dk^2[1 - (c_v/c_p)](\omega^2 - c^2k^2) - (c_v/c_p)\,\Gamma k^2\omega^2}$$

and in the low temperature limit to

$$\omega \cot\ \delta(k, \omega) \cong (c^2k^2 - \omega^2)/\Gamma k^2.$$

F. *Evaluation of the Absorptive Susceptibility*

At higher temperatures, $n(\mathbf{k}, z)$ and $q(\mathbf{k}, z)$ as given in Eqs. (56) and (57) contain both sound wave and diffusion poles. By using the same device as before, we can calculate the absorptive susceptibilities which describe the long wavelength, low frequency response in this more general case. From (56), (57), and (71) we find, for example, that for $T(\mathbf{k})$ and $\mathbf{v}(\mathbf{k})$ equal to zero in the ordinary fluid

$$\begin{aligned}\chi''_{nn}(k,\omega) &= \omega\,\mathrm{Re}[n(\mathbf{k},z)/p(\mathbf{k})]_{z=\omega+i\epsilon}\\ &= n\left.\frac{\partial n}{\partial p}\right|_T \frac{[1-(c_v/c_p)]\,D_Tk^2\omega}{\omega^2+(D_Tk^2)^2} + n\left.\frac{\partial n}{\partial p}\right|_T \frac{\omega c^2k^4\Gamma(c_v/c_p)}{(\omega^2-c^2k^2)^2+(\omega k^2\Gamma)^2}\\ &\quad - n\left.\frac{\partial n}{\partial p}\right|_T \frac{D_T[1-(c_v/c_p)](\omega^2-c^2k^2)\,\omega k^2}{(\omega^2-c^2k^2)^2+(\omega k^2\Gamma)^2}.\end{aligned} \tag{87a}$$

Similarly we find that

$$\chi''_{q,q}(k,\omega) = \frac{nmc_pT\,D_Tk^2\omega}{\omega^2+(D_Tk^2)^2} \tag{87b}$$

and

$$\chi''_{n,q}(k,\omega) = \left.\frac{\partial n}{\partial T}\right|_p \left[\frac{D_Tk^2\omega}{\omega^2+(D_Tk^2)^2} - \frac{D_Tk^2\omega(\omega^2-c^2k^2)}{(\omega^2-c^2k^2)^2+(\omega\Gamma k^2)^2}\right]. \tag{87c}$$

Finally, from (51), it follows that

$$\chi''_{\mathrm{t}}(k,\omega) = \frac{\eta k^2\omega}{\omega^2+(\eta k^2/mn)^2}. \tag{87d}$$

We can sum up our results as follows: In the low wave number, low frequency limit, the correlation function composed of the transverse component of the momentum exhibits a diffusion structure with diffusivity, $D_{\mathrm{t}} = \eta/mn$, given by the viscosity divided by the mass density. The heat energy–heat energy correlation function also has a diffusion structure but here the diffusivity is the thermal diffusivity, $D_T = \kappa/mnc_p$. The density–density correlation function exhibits both this diffusion process and a damped sound wave propagation. The total weight of $\chi''_{n,n}/\omega$ is $n(\partial p/\partial n)_T$ of which a proportion $(1-c_v/c_p)$ comes from the diffusion process and a proportion c_v/c_p comes from the sound propagation. The heat energy–density correlation function also reflects both processes but the sound propagation contributes negligible weight to $\chi''_{n,q}/\omega$.

G. *Expressions for the Transport Coefficients*

In this section, we derive expressions for the transport coefficients: the thermal conductivity, κ, the viscosity, η, and the bulk viscosity, ζ. The expressions we derive are Kubo-type formulas in that they relate the transport coefficients to correlation functions formed of the currents of the conserved operators. The argument that we use is essentially identical to that used in deriving Eq. (44). In that situation, we started from the fact that the spin diffusion coefficient obeyed

$$\lim_{\omega\to 0}\left[\lim_{k\to 0}\frac{\omega}{k^2}\chi''_{M,M}(k,\omega)\right] = D_M\chi_{M,M}.$$

We then applied the spin conservation law to find

$$D_M \chi_{M,M} = \frac{\beta}{4} \lim_{\omega \to 0} \left[\lim_{k \to 0} \int d\mathbf{r} \int dt\, e^{-i\mathbf{k}\cdot\mathbf{r}+i\omega t} \langle \{ j_x{}^M(\mathbf{r}, t), j_x{}^M(\mathbf{0}, 0) \} \rangle \right].$$

According to Eq. (87b),

$$\lim_{\omega \to 0} \left[\lim_{k \to 0} \frac{\omega}{k^2} \chi''_{qq}(k, \omega) \right] = mnc_p T D_T = T\kappa.$$

Therefore, the thermal conductivity can be expressed as

$$\kappa = \frac{\beta}{4T} \lim_{\omega \to 0} \left[\lim_{k \to 0} \int d\mathbf{r} \int dt\, e^{-i\mathbf{k}\cdot\mathbf{r}+i\omega t} \langle \{ j_x{}^q(\mathbf{r}, t), j_x{}^q(\mathbf{0}, 0) \} \rangle. \qquad (88a)$$

However, according to (87a),

$$\lim_{\omega \to 0} \left[\lim_{k \to 0} \frac{\omega}{k^2} \chi''_{n,n}(k, \omega) \right] = 0$$

so that

$$0 = \lim_{\omega \to 0} \left[\lim_{k \to 0} \int d\mathbf{r} \int dt\, e^{-i\mathbf{k}\cdot\mathbf{r}+i\omega t} \langle \{ g_x(\mathbf{r}, t), g_x(\mathbf{0}, 0) \} \rangle \right],$$

and also, according to (87c),

$$\lim_{\omega \to 0} \left[\lim_{k \to 0} \frac{\omega}{k^2} \chi''_{n,q}(k\omega) \right] = 0$$

so that

$$0 = \lim_{\omega \to 0} \left[\lim_{k \to 0} \int d\mathbf{r} \int dt\, e^{-i\mathbf{k}\cdot\mathbf{r}+i\omega t} \langle \{ j_x{}^q(\mathbf{r}, t), g_x(\mathbf{0}, 0) \} \rangle \right].$$

Therefore, not only is the thermal conductivity given by expression (88a); it is also given by the much more general expression

$$\kappa = \frac{\beta}{4T} \lim_{\omega \to 0} \left[\lim_{k \to 0} \int d\mathbf{r} \int dt\, e^{-i\mathbf{k}\cdot\mathbf{r}+i\omega t} \right.$$
$$\left. \times \langle \{ j_x{}^q(\mathbf{r}, t) + \lambda g_x(\mathbf{r}, t), j_x{}^q(\mathbf{0}, 0) + \lambda g_x(\mathbf{0}, 0) \} \rangle \right], \qquad (88b)$$

where λ is any constant. The choice $\lambda=(\epsilon+p)/(mn)$ is particularly instructive since

$$\mathbf{j}^q(\mathbf{r},t)+\frac{\epsilon+p}{mn}\mathbf{g}(\mathbf{r},t)=\mathbf{j}^\epsilon(\mathbf{r},t),$$

where $\mathbf{j}^\epsilon$ is just the energy current. With this choice of λ, the thermal conductivity can be expressed as

$$\kappa=\frac{\beta}{4T}\lim_{\omega\to 0}\left[\lim_{k\to 0}\int d\mathbf{r}\int dt\, e^{-i\mathbf{k}\cdot\mathbf{r}+i\omega t}\langle\{j_x{}^\epsilon(\mathbf{r},t),\, j_x{}^\epsilon(\mathbf{0},0)\}\rangle\right]. \tag{88c}$$

The fact that the thermal conductivity can be represented by either expression (88a) or expression (88c) sheds some light on an apparently puzzling relation between the work of Mori and Green [21]. Both authors worked with $k=0$ from the very beginning of their calculation. Mori used the grand canonical ensemble and found a result of the form of (88a) in which the thermal conductivity is expressed in terms of a correlation function formed with $\mathbf{j}^q$'s. Green used the microcanonical ensemble and found that the thermal conductivity could be represented in the form (88c), in which the correlation function was formed from energy currents. The difference between their two results and Green's explanation of it is rather disturbing since it seems peculiar to ascribe significance to a correlation function whose value depends upon the ensemble used.

Our result complements the results of these two authors. We do not begin with the case in which k is truly set equal to zero since, in this case, not all correlation functions are well defined, and it is true that some depend on the ensemble. The hydrodynamic equations manifest this ensemble dependence through their strong dependence on initial conditions in time and boundary conditions at the edges of the container in which the system is enclosed. However, the hydrodynamic equations indicate that so long as $1/k$ is much smaller than a linear dimension of the container, these complications are irrelevant. As we might expect physically, we can unambiguously associate a transport coefficient with a spontaneous fluctuation function whenever the spontaneous fluctuation function is physically well defined and ensemble independent. This is the case whenever $1/k$ is much smaller than a container dimension but larger than any possible microscopic length. The evaluation of the physical functions in the limit $k\to 0$ is therefore assumed to take place after the container walls have receded to infinity. The limit as $k\to 0$, when the volume is kept finite, is ensemble dependent in a manner which we can understand from the hydrodynamic equations both mathematically and physically. The choice of a correct ensemble and current when $k\to 0$ first is in fact dictated by the requirement that the ensemble and current yield a result in agreement with the ensemble independent limit appropriate for $V\to\infty$ and then $k\to 0$. Under these circumstances, our analysis of the hydrodynamic equations indicates that the thermal conductivity can be expressed in terms of correlations of either $\mathbf{j}^\epsilon$ or $\mathbf{j}^q$. Mori's and Green's discussions each present an ensemble and a current for which no error results from the unphysical limiting process.

Finally, we indicate that we can obtain the standard Kubo-type expressions for the viscosity by employing the facts that from (87d)

$$\lim_{\omega \to 0} \left[\lim_{k \to 0} \frac{\omega}{k^2} \chi''_{\mathrm{t}}(k, \omega) \right] = \eta \tag{89a}$$

and from (87a)

$$\lim_{\omega \to 0} \left[\lim_{k \to 0} \frac{\omega}{k^2} \chi''_{l}(k, \omega) \right] = \lim_{\omega \to 0} \left[\lim_{k \to 0} \frac{m^2 \omega^2}{k^4} \chi''_{n,\, n}(k, \omega) \right] = \frac{4}{3} \eta + \zeta. \tag{89b}$$

Thus,

$$\frac{4}{3} \eta + \zeta = \frac{\beta}{4} \lim_{\omega \to 0} \left[\lim_{k \to 0} \int d\mathbf{r} \int dt \, \frac{\omega^2}{k^4} \langle \{ \mathbf{k} \cdot \mathbf{g}(\mathbf{r}, t), \mathbf{k} \cdot \mathbf{g}(\mathbf{0}, 0) \} \rangle e^{-i\mathbf{k} \cdot \mathbf{r} + i\omega t} \right].$$

Applying the same arguments as before, we find that the viscosity and bulk viscosity may be obtained from the well-known correlation function expression

$$\begin{aligned} &\eta \left(\delta_{ij} - \frac{1}{3} \frac{k_i k_j}{k^2} \right) + \zeta \frac{k_i k_j}{k^2} \\ &\quad = \frac{\beta}{4} \lim_{\omega \to 0} \left[\lim_{k \to 0} \int d\mathbf{r} \int dt e^{-i\mathbf{k} \cdot \mathbf{r} + i\omega t} \sum_{nm} \frac{k_n k_m}{k^2} \langle \{ \tau_{im}(\mathbf{r}, t), \tau_{jn}(\mathbf{0}, 0) \} \rangle \right], \end{aligned} \tag{90}$$

where τ is the stress tensor.

APPENDIX A: PERTURBATION THEORY

In this appendix we remind the reader of the expression which results from using time dependent perturbation theory to describe the effect of an external disturbance. We suppose that prior to time t_0 the state Ψ is a stationary state of the time independent Hamiltonian H. Subsequent to t_0 an external disturbance is applied which couples to the observable properties, $A_j(\mathbf{r}, t)$, of the system. We describe this disturbance by an additional term in the Hamiltonian

$$\mathscr{H}_{\mathrm{ext}} = \int d\mathbf{r} \sum_j A_j(\mathbf{r}, t)\, a_j(\mathbf{r}, t).$$

The functions $a_j(\mathbf{r}, t)$ represent the generalized external forces. For example, the observables might include components of the magnetization, in which case the corresponding force a_j would be the components of the external magnetic field. To calculate the expectation value at time t of the observable A_i we must calculate

$$\langle \Psi(t), A_i^{\mathrm{S}}(\mathbf{r}, t)\, \Psi(t) \rangle, \tag{A.1}$$

where $\Psi(t)$ is the Schroedinger wave function which was equal to Ψ for $t < t_0$ and $A_i^{\mathrm{S}}(\mathbf{r}, t)$ is the operator in the Schroedinger representation which characterizes the observable. Time dependent perturbation theory may be generated by introducing a wave function $\Phi(t)$ at time t_0 which would have become $\Psi(t)$ if no external perturbation had been applied, that is,

$$\Psi(t) \equiv e^{-iH(t-t_0)}\Phi(t).$$

From the Schroedinger equation we obtain

$$\begin{aligned} i\partial\Phi/\partial t &= e^{iH(t-t_0)}H^{\mathrm{S}}_{\mathrm{ext}}(t)\, e^{-iH(t-t_0)}\Phi(t) \\ \Phi(t) &= \Psi(t_0) - i\int_{t_0}^{t} dt' H^{\mathrm{I}}_{\mathrm{ext}}(t')\, \Phi(t'), \end{aligned} \tag{A.2}$$

where for any operator $O^{\mathrm{S}}(t)$, the corresponding interaction representation operator is defined by

$$O^{\mathrm{I}} = e^{iH(t-t_0)}O^{\mathrm{S}}(t)\, e^{-iH(t-t_0)}.$$

The formal solution of Eq. (A.2) is

$$\Psi(t) = e^{-iH(t-t_0)}\left(\exp\left[-i\int_{t_0}^{t} dt' H^{\mathrm{I}}_{\mathrm{ext}}(t')\right]\right)_{+} \Psi(t_0), \tag{A.3}$$

where the formal expression, the ordered product in brackets, is defined by the power series generated by iterating Eq. (A.2). For later purposes we note that direct integration of the equation for Ψ yields the alternative equivalent expression,

$$\begin{aligned} &\exp\left[-i\int_{t_0}^{t} (H + H^{\mathrm{S}}_{\mathrm{ext}}(t'))\, dt'\right]_{+} \\ &\qquad = e^{-iH(t-t_0)}\exp\left[-i\int_{t_0}^{t} H^{\mathrm{I}}_{\mathrm{ext}}(t')\, dt'\right]_{+}. \end{aligned} \tag{A.4}$$

Indeed, it is for this purpose that we have generated the perturbation series in terms of states instead of developing it for the density matrix directly. Substituting into (A.1) we obtain

$$\begin{aligned} \langle \Psi(t), A_i^{\mathrm{S}}(\mathbf{r}, t)\, \Psi(t)\rangle = \Big\langle &\Psi(t_0), \exp\left[i\int_{t_0}^{t} H^{\mathrm{I}}_{\mathrm{ext}}(t')\, dt'\right]_{-} \\ &\times A_j^{\mathrm{I}}(\mathbf{r}, t)\exp\left[-i\int_{t_0}^{t} H^{\mathrm{I}}_{\mathrm{ext}}(t')\, dt'\right]_{+} \Psi(t_0)\Big\rangle. \end{aligned}$$

By expanding the exponential we obtain the result to any desired order. In particular, if we expand to first order, and denote by a bracket the average over an ensemble of stationary states at time t_0, we deduce

$$\langle A_i(\mathbf{r}, t)\rangle = \langle A_i^{\mathrm{I}}(\mathbf{r}, t)\rangle + i\sum_j \int d\mathbf{r}' \int_{t_0}^{t} dt' \times \langle [A_i^{\mathrm{I}}(\mathbf{r}, t), A_j^{\mathrm{I}}(\mathbf{r}', t')]\rangle\, a_j(\mathbf{r}', t'). \tag{A.5}$$

If the observables are not explicitly time dependent in the Schroedinger representation, the operators $A^{\mathrm{I}}(\mathbf{r}, t)$ are the Heisenberg operators for the Hamiltonian H. We shall henceforth assume that this is the case and omit the superscripts I. In terms of the absorptive susceptibility, defined by

$$\tilde{\chi}''_{ij}(r, r'; t-t') \equiv \frac{1}{2}\langle [A_i(\mathbf{r}, t), A_j(\mathbf{r}', t')]\rangle = \int \frac{d\omega}{2\pi} e^{-i\omega(t-t')} \chi''_{ij}(\mathbf{r}, \mathbf{r}'; \omega), \tag{A.6}$$

and the integral representation of the step function

$$\eta(t-t') = \lim_{\epsilon\to 0} i\int \frac{d\omega}{2\pi}\frac{e^{-i\omega(t-t')}}{\omega + i\epsilon} = 0 \qquad \text{for} \quad t<t'$$
$$= 1 \qquad \text{for} \quad t>t',$$

we may write

$$\delta\langle A_i(\mathbf{r}, t)\rangle = \lim_{\epsilon\to 0}\sum_j 2i\int dr' \int_{-\infty}^{\infty} dt' \int \frac{d\bar{\omega}}{2\pi}\frac{ie^{-i\bar{\omega}(t-t')}}{\bar{\omega}+i\epsilon} \times \int \frac{d\omega}{2\pi}\chi''_{ij}(\mathbf{r}, \mathbf{r}'; \omega)\, e^{-i\omega(t-t')} a_j(\mathbf{r}', t').$$

We finally obtain

$$\delta\langle A_i(\mathbf{r}, t)\rangle = \sum_j \int_{-\infty}^{\infty} dt' \int dr' \tilde{\chi}_{ij}(\mathbf{r}, \mathbf{r}'; t-t')\, a_j(\mathbf{r}', t'), \tag{A.7}$$

where $\tilde{\chi}_{ij}(\mathbf{r}, \mathbf{r}'; t-t')$ is the Fourier transform of the complex susceptibility $\chi_{ij}(\mathbf{r}, \mathbf{r}'; \omega)$ and

$$\chi_{ij}(\mathbf{r}, \mathbf{r}'; \omega) = \chi'_{ij}(\mathbf{r}, \mathbf{r}'; \omega) + i\chi''_{ij}(\mathbf{r}, \mathbf{r}'; \omega) \tag{A.8}$$

is the boundary value as z approaches ω on the real axis from above, of the analytic function of z

$$\chi_{ij}(\mathbf{r}, \mathbf{r}'; z) = \int \frac{d\bar{\omega}}{\pi} \frac{\chi''_{ij}(\mathbf{r}, \mathbf{r}'; \bar{\omega})}{\bar{\omega} - z}. \tag{A.9}$$

APPENDIX B: SOME PROPERTIES OF THE COMPLEX SUSCEPTIBILITY

1. *Symmetries*

In the text we noted the symmetry properties of χ''_{ij} for a spatially invariant system (that is for a system invariant under rotations, translations, and inversions) when A_i was the same as A_j. We summarize here the more general symmetry properties.[13]

(a) Since $\tilde{\chi}''_{ij}$ is a commutator, it is antisymmetric under interchange of $\mathbf{r}$ with $\mathbf{r}'$, i with j, and t with t'. We therefore have

$$\begin{aligned} \tilde{\chi}''_{ij}(\mathbf{r}, \mathbf{r}'; t-t') &= -\tilde{\chi}''_{ji}(\mathbf{r}', \mathbf{r}; t'-t) \\ \chi''_{ij}(\mathbf{r}, \mathbf{r}'; \omega) &= -\chi''_{ji}(\mathbf{r}', \mathbf{r}; -\omega). \end{aligned} \tag{B.1}$$

(b) The fact that $\tilde{\chi}''_{ij}$ is the commutator of hermitian operators leads to the identity

$$\begin{aligned} [\tilde{\chi}''_{ij}(\mathbf{r}, \mathbf{r}'; t-t')]^* &= -[\tilde{\chi}''_{ij}(\mathbf{r}, \mathbf{r}'; t-t')] \\ \chi''_{ij}(\mathbf{r}, \mathbf{r}'; \omega) &= -\chi''^{*}_{ij}(\mathbf{r}, \mathbf{r}'; -\omega) = \chi''^{*}_{ji}(\mathbf{r}, \mathbf{r}'; \omega). \end{aligned} \tag{B.2}$$

Thus the part of $\chi''_{ij}(\mathbf{r}, \mathbf{r}'; \omega)$ which is symmetric under interchange of i with j and $\mathbf{r}$ with $\mathbf{r}'$ is both real and odd in ω while the antisymmetric part is imaginary and even in ω. These statements imply in particular that if $\chi_{ii}(\mathbf{r}, \mathbf{r}'; \omega)$ is spatially invariant it is real and odd in the frequency.

(c) A similar result applicable to different operators follows from time reversal. Since the time reversal operator, T, has the property

$$(T\Psi, T\Phi) = (\Phi, \Psi),$$

and for hermitian operators, $A_i(\mathbf{r}, t)$

$$TA_i(\mathbf{r}, t)\, T^{-1} = \epsilon_i A_i(\mathbf{r}, -t),$$

---

[13] It should be noted that all properties of the system are defined in terms of commutators. The corresponding classical relations can be obtained by using the equivalence of the commutator with the Poisson bracket multiplied by i in the correspondence limit. Obviously, this leaves the various symmetry properties unaltered.

where ϵ_i is the signature of the operator A_i under time reversal, we have

$$(\Psi, [A_i(\mathbf{r}, t), A_j(\mathbf{r}', t')]\, \Psi) = \epsilon_i \epsilon_j (T\Psi, [A_j((\mathbf{r}', -t'), A_i(\mathbf{r}, -t)]\, T\Psi).$$

Consequently whenever the Hamiltonian and the ensemble of states are invariant under time reversal

$$\begin{aligned} \tilde{\chi}''_{ij}(\mathbf{r}, \mathbf{r}'; t-t') &= \epsilon_i \epsilon_j \tilde{\chi}''_{ji}(\mathbf{r}', \mathbf{r}; t-t') \\ \chi''_{ij}(\mathbf{r}, \mathbf{r}'; \omega) &= \epsilon_i \epsilon_j \chi''_{ji}(\mathbf{r}', \mathbf{r}; \omega). \end{aligned} \tag{B.3}$$

This means that if A_i and A_j have the same signature under time reversal $\chi''_{ij}(\mathbf{r}, \mathbf{r}'; \omega)$ is odd in ω, real, and symmetric under interchange of i with j and $\mathbf{r}$ with $\mathbf{r}'$. If they have opposite signature, $\chi''_{ij}(\mathbf{r}, \mathbf{r}'; \omega)$ is even, imaginary, and antisymmetric.

If the Hamiltonian and ensemble involve a magnetic field or some other property which changes sign under time reversal, then the relation

$$\chi''_{ij}(\mathbf{r}, \mathbf{r}'; \omega; \mathbf{B}) = \epsilon_i \epsilon_j \chi''_{ji}(\mathbf{r}', \mathbf{r}; \omega; -\mathbf{B}) \tag{B.3$'$}$$

is obtained. Hence for two operators with the same signature under time reversal there will be an additional part of $\chi''_{ij}(\mathbf{r}, \mathbf{r}'; \omega)$ which is odd in the field, $\mathbf{B}$, even in ω, imaginary, and antisymmetric in i, $\mathbf{r}$ and j, $\mathbf{r}'$.

The symmetry properties of $\chi'_{ij}(\mathbf{r}, \mathbf{r}'; \omega; \mathbf{B})$ are determined from the relation

$$\chi'_{ij}(\mathbf{r}, \mathbf{r}'; \omega; \mathbf{B}) = \mathscr{P} \int \frac{d\bar{\omega}}{\pi} \frac{\chi''_{ij}(\mathbf{r}, \mathbf{r}'; \bar{\omega}; \mathbf{B})(\bar{\omega} + \omega)}{\bar{\omega}^2 - \omega^2} \tag{B.4}$$

which means that they are identical apart from the interchange of evenness and oddness in ω.

2. *Sum Rules and Moment Expansions*

The moment sum rule discussed in the text is the first of a sequence of statements

$$\left\langle \left[\frac{d^n A_i(\mathbf{r}, t)}{dt^n}, A_j(\mathbf{r}', t') \right] \right\rangle \bigg|_{t'=t} = \int \frac{d\bar{\omega}}{\pi} (-i\bar{\omega})^n \chi''_{ij}(\mathbf{r}, \mathbf{r}'; \bar{\omega}). \tag{B.5}$$

These statements and the Kramers–Kronig relation (B.4) give rise to a moment expansion, valid at high frequencies,

$$\begin{aligned} \chi'_{ij}(\mathbf{r}, \mathbf{r}'; \omega) &= -\sum_n \int \frac{d\bar{\omega}}{\pi} \left(\frac{\bar{\omega}}{\omega} \right)^n \frac{\chi''_{ij}(\mathbf{r}, \mathbf{r}'; \omega)}{\omega} \\ &= \sum_n \frac{i^n}{\omega^{n+1}} \left\langle \left[-\frac{d^n A_i(\mathbf{r}, t)}{dit^n}, A_j(\mathbf{r}, t') \right] \right\rangle \bigg|_{t=t'}. \end{aligned} \tag{B.6}$$

3. *Identification of χ'' with Dissipation*

The rate at which mechanical work is done on a system by an external force is equal to the explicit rate of change in the Hamiltonian

$$\frac{dW}{dt}=-\sum_{i,\,j}\int \dot{a}_i(\mathbf{r},t)\,\tilde{\chi}_{ij}(\mathbf{r},\mathbf{r}';t-t')\,a_j(\mathbf{r}',t')\,dt'\,dr\,dr'.$$

The mechanical dissipation (which is equal to the entire dissipation at constant entropy) is obtained by integrating this expression over time.

$$\int dW=\sum_{i,\,j}\int d\mathbf{r}\int d\mathbf{r}'a_i(\mathbf{r},t)\left[\frac{\partial}{\partial t}\chi_{ij}(\mathbf{r},\mathbf{r}';t-t')\right]a_j(\mathbf{r}',t')\,dt\,dt'. \tag{B.7}$$

Since $\partial\chi'/\partial t$ is antisymmetrical in time and $\partial\chi''/\partial t$ is symmetrical, only $\partial\chi''/\partial t$ contributes to the dissipation. Alternatively, for a single frequency of applied field

$$H_{\text{ext}}(t)=-\int d\mathbf{r}\sum_i A_i(\mathbf{r},t)\,\operatorname{Re}a_i(\mathbf{r})\,e^{-i\omega t}$$

and the mean value of the work done is

$$\overline{\frac{dW}{dt}}=-\frac{1}{2}\operatorname{Re}\sum_{ij}\int d\mathbf{r}\,d\mathbf{r}'a_i{}^*(\mathbf{r})\,i\omega\chi_{ij}(\mathbf{r},\mathbf{r}';\omega)\,a_j(\mathbf{r}').$$

Since χ' and χ'' are both hermitian the average comes only from χ''_{ij}

$$\overline{\frac{dW}{dt}}=\frac{1}{2}\sum_{ij}\int d\mathbf{r}\,d\mathbf{r}'\;a_i{}^*(\mathbf{r})\,\chi''_{ij}(\mathbf{r},\mathbf{r}';\omega)\,a_j(\mathbf{r}')\,\omega. \tag{B.8}$$

We may also write this expression for the rate of energy exchange as the energy, ω, times the difference between transition probabilities for absorption and emission

$$=\frac{\omega}{4}\sum_{ij}\int d\mathbf{r}\,d\mathbf{r}'\int dt e^{i\omega t}a_i{}^*(\mathbf{r})\langle[A_i(\mathbf{r},t),A_j(\mathbf{r}',0)]\rangle a_j(\mathbf{r}')$$

$$=\omega\int dt e^{i\omega t}\int dEw(E)\int dE'\rho(E')$$

$$\cdot\left\{\left|\left\langle\left|\frac{1}{2}\int d\mathbf{r}\sum_i a_i(\mathbf{r})\,A_i(\mathbf{r},0)\right|E'\right\rangle\right|^2(e^{i(E-E')t}-e^{-i(E-E')t})\right\},$$

where $\rho(E')$ is the density of states of the Hamiltonian and $w(E)$ the normalized weighting of states of the stationary ensemble. In writing this equation and the subsequent equations (B.9) and (B.14), we have assumed that the states may be labeled by the energy alone, that is, that there is no degeneracy. When the states are degenerate, these equations should include averages over states of identical energy. This extra averaging process changes none of our conclusions. We therefore obtain

$$
\begin{aligned}
&= \omega \left\{ 2\pi \int dE w(E) \left| \left\langle E \left| \tfrac{1}{2} \sum_i \int d\mathbf{r} a_i(\mathbf{r})\, A(\mathbf{r}, 0) \right| E + \omega \right\rangle \right|^2 \rho(E+\omega) \right. \\
&\quad \left. - 2\pi \int dE w(E) \left| \left\langle E \left| \tfrac{1}{2} \sum_i \int dr a_i(\mathbf{r})\, A_i(\mathbf{r}, 0) \right| E - \omega \right\rangle \right|^2 \rho(E-\omega) \right\}.
\end{aligned}
$$

The rate of change of mechanical energy may of course be associated with the rate of change of free energy in an ensemble at constant temperature. Since the matrix $\chi''_{ij}\omega$ describes the dissipation it must be positive definite in any stable system. This positive definiteness of $\omega\chi''_{ij}(\mathbf{r}, \mathbf{r}'; \omega)$ has implications for $\chi'_{ij}(\mathbf{r}, \mathbf{r}'; \omega)$. In particular it follows from Eq. (B.4) that $\chi'_{ij}(\mathbf{r}, \mathbf{r}'; \omega)$ is a nonnegative matrix at vanishing frequency. Hence, for example, the static electric polarizability must be positive. Likewise, for the one-component fluid discussed in the text, this requirement reduces in the long wavelength limit to the familiar thermodynamic stability conditions $(dp/dn)_S > 0$, $c_p > 0$, and $(dp/dn)_T > 0$.

Note also that at large frequencies the "sign" of the matrix χ'_{ij} is always negative. This behavior is just what we expect for an oscillator bound by a restoring force $n\omega_0{}^2$ and perturbed by an external force of frequency, ω. Its displacement will be 180° out of phase with the force when $\omega \gg \omega_0$ and the absorption is sufficiently small so that there is oscillation (that is, when we have an oscillator damped less than critically); also the absorption will be maximum at an intermediate frequency when the displacement is out of phase with the force by 90°. Although we shall not pursue the point, it should be clear that in the representation in which $\chi_{ij}(\mathbf{r}, \mathbf{r}'; \omega)$ is diagonalized, its logarithm gives a natural definition for frequency-dependent phase shifts in precise analogy with the above description and the phase shift representation discussed in connection with the dispersion relation for magnetic susceptibility.

4. *Fluctuation Dissipation Theorem*

The time translation property of the weighting factor for a canonical ensemble and the cyclical property of the trace imply the identities

$$
\begin{aligned}
\operatorname{Tr} e^{-\beta H} A_i(\mathbf{r}, t)\, A_j(\mathbf{r}', t') &= \operatorname{Tr} A_i(\mathbf{r}, t + i\beta)\, e^{-\beta H} A_j(\mathbf{r}', t') \\
&= \operatorname{Tr} e^{-\beta H} A_j(\mathbf{r}', t')\, A_i(\mathbf{r}, t + i\beta). \qquad \text{(B.10)}
\end{aligned}
$$

Moreover $\operatorname{Tr}[\exp(-\beta H)\, A(\mathbf{r}, t)]$ is independent of time. Consequently, provided the time Fourier transform

$$
\frac{1}{2} \langle [A_i(\mathbf{r}, t) - \langle A_i(\mathbf{r}, t) \rangle][A_j(\mathbf{r}, t) - \langle A_j(\mathbf{r}, t) \rangle] \rangle = \int \frac{d\omega}{2\pi} f_{ij}(\mathbf{r}, \mathbf{r}'; \omega)\, e^{-i\omega(t-t')}
$$

exists, it satisfies

$$f_{ij}(\mathbf{r}, \mathbf{r}'; \omega) = f_{ji}(\mathbf{r}', \mathbf{r}; -\omega)\, e^{\beta\omega}$$

and therefore,[14]

$$\chi''_{ij}(\mathbf{r}, \mathbf{r}'; \omega) = (1 - e^{-\beta\omega})\, f_{ij}(\mathbf{r}, \mathbf{r}'; \omega) = (e^{\beta\omega} - 1)\, f_{ji}(\mathbf{r}', \mathbf{r}; -\omega). \tag{B.11}$$

Likewise the transform of the symmetrized product

$$\frac{1}{2} \langle \{ [A_i(\mathbf{r}, t) - \langle A_i(\mathbf{r}, t) \rangle], [A_j(\mathbf{r}', t') - \langle A_j(\mathbf{r}', t') \rangle] \} \rangle$$

$$= \int \frac{d\omega}{2\pi} s_{ij}(\mathbf{r}, \mathbf{r}'; \omega)\, e^{-i\omega(t-t')} \tag{B.12}$$

satisfies the identity

$$s_{ij}(\mathbf{r}, \mathbf{r}'; \omega) = (1 + e^{\beta\omega})\, f_{ij}(\mathbf{r}, \mathbf{r}'; \omega)$$

and the fluctuation dissipation theorem[15]

$$\begin{aligned} \frac{1}{2} s_{ij}(\mathbf{r}, \mathbf{r}'; \omega) &= \omega \left[\frac{1}{2} + \frac{1}{e^{\beta\omega} - 1} \right] \frac{\chi''_{ij}(\mathbf{r}, \mathbf{r}'; \omega)}{\omega} \\ &= \frac{1}{2} \coth \frac{\beta\omega}{2}\, \chi''_{ij}(\mathbf{r}, \mathbf{r}'; \omega). \end{aligned} \tag{B.13}$$

We may use the expression (B.8) for the dissipation and (B.13) to demonstrate that our statement of stability

$$W = \tfrac{1}{2} \sum_{ij} \int d\mathbf{r}\, d\mathbf{r}'\, a_i{}^*(\mathbf{r})\, \chi''_{ij}(\mathbf{r}, \mathbf{r}'; \omega)\, a_j(\mathbf{r})\, \omega \geqq 0$$

is satisfied by the canonical ensemble. For this purpose, with the aid of Eq. (B.13) it is only necessary to show that the fluctuations at a single frequency are positive definite. By introducing a set of intermediate states we obtain

$$\begin{aligned} W = \tfrac{1}{2}\omega \tanh \tfrac{1}{2}\beta\omega \int dE w_{\text{eq.}}(E) \int dE' \rho(E') [\delta(E' - E + \omega) + \delta(E' - E - \omega)] \\ \times 2\pi \left| \left\langle E \left| \sum_i \int d\mathbf{r} a_i(\mathbf{r}) [A_i(\mathbf{r}, 0) - \langle A_i(\mathbf{r}, 0) \rangle] \right| E' \right\rangle \right|^2 \geqq 0, \end{aligned} \tag{B.14}$$

where $w_{\text{eq.}}(E)$ is the normalized distribution for the equilibrium ensemble.

---

[14] This is the first relation in the appendices which depends on canonical averaging. We shall subsequently assume this particular density matrix.

[15] Had Poisson brackets and classical mechanics been employed, this relation would have involved $2/\beta\omega$ instead of $\coth(\beta\omega/2)$.

APPENDIX C: RELAXATION

In this final appendix we make explicit the connection of our discussion with the widely quoted peculiar looking dissipation function of Kubo. We also demonstrate how the latter arises directly in a discussion of relaxation and leads alternatively to the expression for relaxation discussed in the text. We recall a familiar parallel. In classical electromagnetic theory we use the retarded Green's function for the wave equation to determine the radiation emitted by charges moving along prescribed trajectories. We also use this function to find the behavior of radiation in free space in terms of the radiation present at an initial time. The former corresponds to the characterization of the response to externally applied forces. The latter corresponds to the relaxation problem we shall now discuss. It would clearly be possible to consider simultaneously emission of radiation by charges undergoing prescribed motions and the propagation and absorption of incident radiation present initially. Likewise it would be possible to discuss a system relaxing to equilibrium and simultaneously subjected to external forces. Since there is no really new effect we shall confine ourselves to free relaxation.

We suppose that initially the system is characterized by a disturbed density matrix

$$\rho = \Xi[\mathrm{Tr}\,\Xi]^{-1},$$

where

$$\begin{aligned}\Xi &\equiv \exp\left[-\beta H + \beta \sum_j \int d\mathbf{r}'\, A_j(\mathbf{r}')\, a_j(\mathbf{r}')\right]\\ &\equiv \exp[-\beta(H + H_{\mathrm{ext}})].\end{aligned} \tag{C.1}$$

Note particularly that although we have again used the symbol H_{ext} it here describes an initial condition and does not depend on the time in any way. For times $t > 0$, a property A_i of the system transforms according to

$$A_i(\mathbf{r}, t) = e^{iHt} A_i(\mathbf{r})\, e^{-iHt}.$$

Thus we have

$$\langle A_i(\mathbf{r}, t)\rangle_{\mathrm{noneq.}} = \mathrm{Tr}[A_i(\mathbf{r}, t)\, \rho]. \tag{C.2}$$

We now employ a special form of the identity (A.4)

$$\begin{aligned}\exp[-\beta(H + H_{\mathrm{ext}})] &= \exp(-\beta H)\, \exp\left(-\int_0^\beta H^{\mathrm{I}}_{\mathrm{ext}}(-i\beta')\, d\beta'\right)_+\\ H^{\mathrm{I}}_{\mathrm{ext}}(-i\beta') &= \exp(\beta' H)\, H_{\mathrm{ext}}\, \exp(-\beta' H).\end{aligned} \tag{C.3}$$

To first order in H_{ext}, we obtain from Eqs. (C.1)–(C.3)

$$\delta\langle A_i(\mathbf{r}, t)\rangle = \sum_j \int d\mathbf{r}' \int_0^\beta d\beta' [\langle A_j(\mathbf{r}', -i\beta')\, A_i(\mathbf{r}, t)\rangle_{\text{eq.}} - \langle A_j(\mathbf{r}', -i\beta)\rangle_{\text{eq.}} \langle A_i(\mathbf{r}, t)\rangle_{\text{eq.}}]\, a_j(\mathbf{r}'). \tag{C.4}$$

Taking into account the relaxation between the unordered products and the commutator (B.11) we obtain

$$\begin{aligned}\delta\langle A_i(\mathbf{r}, t)\rangle &= \sum_j \int d\mathbf{r}' \int_0^\beta d\beta' \int \frac{d\omega}{\pi} \frac{\chi''_{ij}(\mathbf{r}, \mathbf{r}'; \omega)}{e^{\beta\omega} - 1} e^{-i\omega(t+i\beta')} a_j(\mathbf{r}') \\ &= \sum_j \int d\mathbf{r}' \int \frac{d\omega}{\pi} \frac{e^{-i\omega t}}{\omega} \chi''_{ij}(\mathbf{r}, \mathbf{r}'; \omega)\, a_j(\mathbf{r}'). \end{aligned}\tag{C.5}$$

Thus the Kubo expression (C.4) is a peculiar way of writing the ensemble averaged commutator, that is to say

$$\int_0^\beta \langle \dot{A}_i(\mathbf{r}, t)\, A_j(\mathbf{r}, i\beta')\rangle_{\text{eq.}}\, d\beta' = -i\langle [A_i(\mathbf{r}, t), A_j(\mathbf{r}', 0)]\rangle_{\text{eq.}} \tag{C.6}$$

Since these expressions apply for $t > 0$ it is natural to introduce one-sided Fourier transforms as in the text and write

$$A_i(\mathbf{r}, z) = -\frac{1}{iz} \sum_j \int d\mathbf{r}' \left[\int \frac{d\omega}{\pi} \frac{\chi''_{ij}(\mathbf{r}, \mathbf{r}'; \omega)}{\omega} - \chi_{ij}(\mathbf{r}, \mathbf{r}'; z) \right] a_j(\mathbf{r}'). \tag{C.7}$$

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