

attention recently, and seen so much progress. These phenomena can be treated in the language presented here but require a whole array of techniques not covered here.

Moreover, this is not a text about Green's functions and the elaborate techniques usually combined under that label. (See Kadanoﬀ and Baym 1962, Fetter and Walecka 1971.) Green's function methods are methods to perform detailed microscopic calculations, calculations which are always diﬃcult, and often hard to check. It is useful therefore and desirable to obtain, from fundamental principles, constraints on such calculations. Most of the correlation functions which we will discuss here are in fact closely related to one- and two-particle Green's functions. And the results which we will derive -- sum rules, hydrodynamic limiting expressions and others -- provide restrictions which any fully microscopic theory must fulfill.

We will therefore, even when dealing with specific examples, concentrate on the structural aspects of the theory, aim at results which bridge the gap between microscopic equations of motion and macroscopically observable phenomena, and provide a common language in which experiments can be discussed that are performed on a wide variety of physical systems and with a similar variety of methods. A language which should be convenient for him or her who, when analyzing light scattering data from liquid crystals, would like to draw on knowledge of antiferromagnets or superﬂuids. The language of correlation functions is mathematical, of course, but a determined effort has been made to concentrate on the physical ideas involved, and tread lightly on questions of mathematical rigor. If I have succeeded, those who do the real work, the experimentalists, should find in this text a useful and intelligible bit of theory, and hopefully have some fun while reading it.

## CHAPTER 2

### A SIMPLE EXAMPLE -- SPIN DIFFUSION

As a simple example which illustrates many of the points we shall discuss, let us consider a ﬂuid of uncharged particles with spin  $1/2$  (Kadanoﬀ and Martin 1963). The essential assumption which makes this system so simple, is that the particles interact through a velocity- and spin-independent force. This situation is, in fact, realized to an excellent approximation in at least one real system, liquid He<sup>3</sup>. (Much of the subsequent analysis will, however, also apply to the isotropic Heisenberg paramagnet, for example. See chapter 8 and e.g., Bennett and Martin [1965] and Lubensky [1970a].)

The spin of each particle can be taken to point either parallel (+) or antiparallel (-) to some arbitrary direction of quantization. In order to simplify things we will treat the spin as a scalar quantity; its vector character is of no importance for our purposes. The magnetization,  $M(\vec{r}, t)$ , is then simply proportional to the difference in densities  $n_+(\vec{r}, t)$  and  $n_-(\vec{r}, t)$  at the space-time point  $\vec{r}, t$ , i.e.,

$$M(\vec{r}, t) = \mu [n_+(\vec{r}, t) - n_-(\vec{r}, t)], \quad (2.1)$$

where  $\mu$  is the spin magnetic moment of a particle. A more microscopic way of writing this operator is

$$M(\vec{r}, t) = \sum_{\alpha} 2\mu s^{\alpha} \delta(\vec{r} - \vec{r}^{\alpha}(t)), \quad (2.2)$$

where the  $\alpha$ -th particle has the position  $\vec{r}^\alpha(t)$  at time  $t$  and the spin  $s^\alpha$  which is either  $1/2$  or  $-1/2$ . The  $\delta$ -function sees to it that only those particles are counted which at time  $t$  are found at or near the point  $\vec{r}$ . The assumption of spin-independent forces is reflected in the fact that  $s^\alpha$  is constant in time.

In thermal equilibrium,  $n_+ = n_-$  on the average so that  $M = 0$ . Now assume that at some initial time,  $t = 0$ , there is a local imbalance at point  $\vec{r}$  so that  $M(\vec{r}, t=0) \neq 0$ . We will be interested in the subsequent time development of  $M(\vec{r}, t)$ . In our simple model which neglects spin-flip processes, the time dependence of  $M(\vec{r}, t)$  will be due to the fact that the particles move around, carrying their spin with them. In fact it does not much matter what they carry, i. e., what "spin up" and "spin down" mean. A system of green ( $s^\alpha = \frac{1}{2}$ ) and red ( $s^\alpha = -\frac{1}{2}$ ) particles would behave in the same way.

Since  $\vec{r}^\alpha = \vec{p}^\alpha/m$  where  $\vec{p}^\alpha$  is the momentum of the  $\alpha$ -th particle and  $m$  is its mass, we get from (2.2) the continuity equation

$$\partial_t M(\vec{r}, t) + \vec{\nabla} \cdot \vec{j}^M(\vec{r}, t) = 0, \quad (2.3)$$

where  $\vec{j}^M$  is the magnetization current. It can be written in the form

$$\vec{j}^M(\vec{r}, t) = \sum_{\alpha} (\mu s^\alpha / m) \left\{ \vec{p}^\alpha(t), \alpha(\vec{r} - \vec{r}^\alpha(t)) \right\}. \quad (2.4)$$

We will always use curly brackets for the anticommutator

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

For classical particles, the symmetrization in (2.4) is, of course, unnecessary.

Eq. (2.3) expresses the fact that the total magnetization is conserved,

$$\frac{d}{dt} \int d\vec{r} M(\vec{r}, t) = 0, \quad (2.5)$$

but it implies an important additional property: the current  $\vec{j}^M(\vec{r}, t)$ , as the

magnetization  $M(\vec{r}, t)$ , is a local density, dependent only on properties of particles which, at time  $t$ , are in some small neighborhood around the point  $\vec{r}$ . Differential conservation laws like (2.3) will play an important role in most of the processes which we shall discuss.

### 2.1 Hydrodynamic Description

The conservation law (2.3) is not a complete description; it just restricts the dynamics a little. To solve for  $M(\vec{r}, t)$ , we need a second equation relating  $\vec{j}^M$  to  $M$ . Now both  $n_+(\vec{r}, t)$  and  $n_-(\vec{r}, t)$  tend towards an equilibrium state in which they are spatially uniform. In other words, there is a net flow of magnetization from regions of large  $M$  to regions of small  $M$ . Phenomenologically,

$$\langle \vec{j}^M(\vec{r}, t) \rangle = -D \vec{\nabla} \langle M(\vec{r}, t) \rangle. \quad (2.6)$$

This is called a constitutive equation. The transport coefficient,  $D$ , is called the spin diffusion coefficient, and it is positive. Note that while (2.3) is microscopically exact, (2.6) can be true only on the average which is why we have put brackets  $\langle \rangle$  around it. These indicate here a non-equilibrium average, of course; in thermal equilibrium,  $\langle M(\vec{r}, t) \rangle_{\text{eq}}$  is independent of  $\vec{r}, t$ , and  $\langle \vec{j}^M(\vec{r}, t) \rangle_{\text{eq}}$  vanishes.

Inserting (2.6) in (2.3) we get the familiar diffusion equation,

$$\partial_t \langle M(\vec{r}, t) \rangle - D \nabla^2 \langle M(\vec{r}, t) \rangle = 0, \quad (2.7)$$

which is now complete and can be solved. Note that this equation is only valid if all the properties of the system vary slowly in space and time. This assumption is clearly implicit in (2.6), and will be analyzed a little further below.

We are only interested here in an infinitely extended system. This eliminates boundary conditions so that (2.7) is trivially solved by performing a Fourier transformation in space.

$$\langle M(\vec{k}, t) \rangle = \int d\vec{r} e^{-i\vec{k}\cdot\vec{r}} \langle M(\vec{r}, t) \rangle, \quad (2.8a)$$

and a Laplace transformation in time,

$$\langle M(\vec{k}, z) \rangle = \int_0^{\infty} dt e^{izt} \langle M(\vec{k}, t) \rangle. \quad (2.8b)$$

$\vec{k}$  is the wave vector of the fluctuation. The complex frequency  $z$  must lie in the upper half of the complex plane for the integral in (2.8b) to converge. From eq. (2.7) we then obtain

$$\langle M(\vec{k}, z) \rangle = \frac{i}{z + iDk^2} \langle M(\vec{k}, t=0) \rangle, \quad (2.9)$$

which solves the initial value problem.

The diffusion process is reflected in a pole on the negative imaginary axis, at  $z = -iDk^2$ . To get a little more familiar with diffusion poles, note that (2.9) says the same as

$$\langle M(\vec{k}, t) \rangle = e^{-Dk^2 t} \langle M(\vec{k}, t=0) \rangle. \quad (2.10)$$

This equation displays the characteristic property of a "hydrodynamic" mode: it is a spatially sinusoidal collective fluctuation which for large wavelength  $\lambda = 2\pi/k$  is exponentially damped, with a lifetime

$$\tau(k) = 1/Dk^2 \quad (2.11)$$

which becomes infinite as  $k \rightarrow 0$ .

It is well to appreciate that this behavior is very unusual in as chaotic a many-body system as a liquid. There is an enormous number of channels available into which an arbitrary degree of freedom can decay after the initial excitation.

Most degrees of freedom will relax within a short time  $\tau_c$  which is determined by the microscopic interactions. For a system of classical particles of mass  $m$ , inter-

acting with a pair potential of strength  $\epsilon$  and range  $a$ , dimensional arguments suggest that  $\tau_c$  is of the order

$$\tau_c \sim (a^3 m / \epsilon)^{1/2}, \quad (2.12)$$

which for Helium would give  $\tau_c \approx 10^{-12}$  sec. Even though, in a quantum liquid like He<sup>3</sup> at low temperatures, the Pauli principle severely restricts the number of decay channels--dimensionally, the small thermal energy  $k_B T$  and  $\tau_c$  become available to correct (2.12)--the microscopic decay times at all but the very lowest temperatures are still very small on a macroscopic scale.

What is special about the degree of freedom described by  $M(\vec{k}, t)$  is that the magnetization is a conserved quantity. A local excess of this quantity cannot disappear locally (which could happen rapidly) but can only relax by spreading slowly over the entire system. A sinusoidal fluctuation as depicted in fig. 2.1

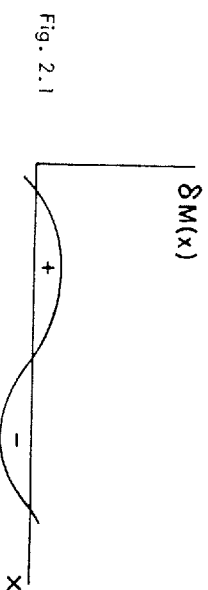


Fig. 2.1

can only relax by the magnetization being physically transported from the excess to the deficiency regions over a distance of order  $\lambda/2$ , a process that requires an infinitely long time as  $\lambda \rightarrow \infty$ . Indeed, if the transport process occurs via a random walk, then  $(\Delta x)^2 \approx Dt$  or  $\tau \approx \lambda^2/D$  which is what we found in (2.11).

Returning to eq. (2.10), let us assume that initially, the magnetization is non-zero only at  $\vec{r} = 0$ , i.e., that  $\langle M(\vec{r}, t=0) \rangle = M\delta(\vec{r})$ . Then

$$\langle M(\vec{r}, t) \rangle = M(4\pi Dt)^{-3/2} \exp(-r^2/Dt), \quad (2.13)$$

which displays the characteristic Gaussian spreading of a random walk process.

### 2.2 Spin Correlation Function (Roughly)

The last few equations solve the problem of spin diffusion in an infinitely extended system. Now, since this is a book about correlation functions, let us try to extract some information about the spin correlation function. We begin by defining the magnetization correlation function by

$$S(\vec{r}, t) = \langle M(\vec{r}, t) M(\vec{0}, 0) \rangle_{\text{eq}}, \quad (2.14)$$

where  $M(\vec{r}, t)$  is the magnetization operator employed above. The average in (2.14) is a thermal equilibrium average, by contrast to the average in (2.6) which is meant to describe a system not yet in full equilibrium. Of course, even though  $\langle M(\vec{r}, t) \rangle_{\text{eq}} = 0$ , there will be spontaneous, usually small, fluctuations on a local scale.  $S(\vec{r}, t)$  describes these fluctuations. Because of the magnetic interaction of neutrons with local magnetization fluctuations, the function  $S(\vec{r}, t)$  can be measured by magnetic neutron scattering.

$S(\vec{r}, t)$  presumably vanishes rapidly when  $r$  and/or  $t$  are very large since then,  $M(\vec{r}, t)$  and  $M(\vec{0}, 0)$  are statistically independent so that  $\langle M(\vec{r}, t) M(\vec{0}, 0) \rangle = \langle M(\vec{r}, t) \rangle \langle M(\vec{0}, 0) \rangle = 0$ . Therefore, it can be Fourier transformed,

$$S(k_{\parallel}) = \int_{-\infty}^{\infty} dt \int d\vec{r} e^{i\vec{r} \cdot \vec{k} - ik_{\parallel} t} S(\vec{r}, t). \quad (2.15)$$

This function represents the spectral density of magnetization fluctuations, and is real and positive. Because of the rotational invariance of the system,  $S(k_{\parallel})$  depends only on the magnitude of  $\vec{k}$ . Of use is also the one-sided (Laplace) transform

$$\tilde{S}(kz) = \int_0^{\infty} dt e^{izt} S(k, t), \quad \text{for } \text{Im}z > 0. \quad (2.16)$$

It is an easy exercise to show that

### 2.2 Spin Correlation Function

$$\tilde{S}(kz) = \int_{\mathcal{C}} \frac{dz'}{2\pi i} \frac{S(kz')}{z' - z}, \quad (2.17)$$

which last equation has a meaning for  $z$  in both the upper and lower halves of the complex plane.  $\tilde{S}(kz)$  is a complex function, analytic in  $z$  except for a branch cut along the real axis. In fact, using the identity

$$\frac{1}{x \pm i\epsilon} = P \frac{1}{x} \pm i\pi \delta(x) \quad (2.18)$$

where  $\epsilon$  is, here and throughout this book, positive and infinitesimal, and  $P$  indicates the Cauchy principal value, we find that  $S(k_{\parallel})$  is the discontinuity across the branch line,

$$S(k_{\parallel}) = \lim_{\epsilon \rightarrow 0} [\tilde{S}(k, x+i\epsilon) - \tilde{S}(k, x-i\epsilon)]. \quad (2.19)$$

More useful is the equation which follows from the reality of  $S(k_{\parallel})$ , namely

$$S(k_{\parallel}) = 2 \text{Re} \tilde{S}(k, x+i\epsilon). \quad (2.20)$$

Now let us first use a hit-and-run technique to obtain the correlation function from our hydrodynamic analysis. Why would we want to do that? First and importantly because the correlation function is of immediate experimental interest since it gives the intensity distribution measured by inelastic neutron scattering. Second, because  $S(\vec{r}, t)$  is a mathematically and operationally well-defined object; we know, in principle at least, how to perform thermal equilibrium averages as in eq. (2.14). The phenomenological fluctuation  $\langle M(\vec{r}, t) \rangle_{\text{non-eq}}$  of section 2.1 is a little more hazy an object since it is harder to give precise meaning to the non-equilibrium average.

What we shall assume is that the constitutive equation (2.6) and therefore the diffusion equation (2.7) are valid, in some sense, even if we omit the average

signs  $\langle \dots \rangle_{\text{non-eq}}$ , i. e., that they can be understood as operator equations. If so, all we have to do is to multiply eq. (2.7) (without the brackets) from the right by  $M(\vec{0}, 0)$  and then do an equilibrium average, to obtain

$$[\partial_t - D\nabla^2] S(\vec{r}, t) = 0. \quad (2.21)$$

Our rough assumption therefore says that spontaneous equilibrium fluctuations--described by  $S$ --relax according to the same diffusion equation as do induced non-equilibrium fluctuations--described by  $\langle M \rangle_{\text{non-eq}}$ . This entirely reasonable hypothesis was first proposed by Onsager (1931), and it is quite correct.

Eq. (2.21) is solved just like (2.7) was, and the result is

$$\tilde{S}(k, z) = \frac{i}{z + iDk^2} S(k, t=0). \quad (2.22)$$

Note, however, that the initial condition is now not arbitrary but is perfectly well defined by eq. (2.14). In fact, in section 2.4 we will show that  $S(k \rightarrow 0, t=0)$  is  $k_B T$  times the spin magnetic susceptibility  $\chi$ ,

$$\lim_{k \rightarrow 0} S(k, t=0) = \beta^{-1} \chi \quad (2.23)$$

and therefore, for small  $k$ ,

$$\tilde{S}(k, z) = \frac{i\beta^{-1} \chi}{z + iDk^2}. \quad (2.24)$$

To extract the spectral density, we cannot use (2.19) since (2.24) holds, by derivation, only for  $\text{Im} z > 0$ . However, we can use (2.20) and obtain the final result

$$S(k, \omega) = \frac{Dk^2}{\omega^2 + (Dk^2)^2} \frac{\beta^{-1} \chi}{\beta \chi}, \quad (2.25)$$

whose experimental significance we shall discuss below.

Of course, eq. (2.25) is an approximation to the real world. It is valid only for small  $k$  and  $\omega$  which means, in the loose language that is common, it is valid when  $k^{-1}$  is much larger than all "natural lengths in the system," and when  $\omega^{-1}$  is much larger than all "natural times in the system". The important length is the mean free path, which in a liquid is of the order of the interparticle distance.

Note that the behavior of the correlation function at small  $k$  and  $\omega$  is by no means simple. For example,  $\lim_{\omega \rightarrow 0} [\lim_{k \rightarrow 0} S(k, \omega)] = 0$  but  $\lim_{k \rightarrow 0} [\lim_{\omega \rightarrow 0} S(k, \omega)] = \infty$ . The order of the limits matters, and one must be extremely careful if he wants to make expansions of correlation functions in terms of  $k$  and  $\omega$ . However, the inverse of the complex function  $\tilde{S}(k, z)$ ,

$$\tilde{S}^{-1}(k, z) = (i\beta^{-1} \chi)^{-1} [z + iDk^2], \quad (2.26)$$

looks smooth, like the beginning of a Taylor series in  $k$  and  $z$ . We shall see that the rational thing to do is usually to make approximations for  $\tilde{S}^{-1}$  rather than  $S$ .

Equation (2.23) is equivalent to

$$\lim_{k \rightarrow 0} \beta \int \frac{d^3x}{2\pi} S(k, \omega) = \chi. \quad (2.27)$$

This is called a thermodynamic sum rule since it gives a thermodynamic derivative,  $\chi = (dM/dH)$  which is the spin magnetic susceptibility, from a frequency integral over the correlation function. This sum rule is exact and our hydrodynamic approximation (2.25) exhausts it.

Furthermore, from (2.25) we see that

$$\frac{\beta}{2} \lim_{\omega \rightarrow 0} [\lim_{k \rightarrow 0} \frac{\omega^2}{k^2} S(k, \omega)] = D \chi, \quad (2.28)$$

which gives the spin diffusion coefficient  $D$  in terms of the correlation function.

This is a Kubo relation though it doesn't quite look like Kubo's original expression

(Kubo 1957). However, it is a simple and useful exercise to manipulate eq. (2.28) into the form

$$D\chi = (\beta/2) \frac{1}{\beta} \int_{-\infty}^{\infty} d\tau \int_{-\infty}^{\infty} dt \langle \vec{M}(\vec{r}, t) \vec{M}(\vec{0}, 0) \rangle, \quad (2.29a)$$

where use is made of translational and rotational invariance. Or finally, defining the total magnetization current operator by

$$\vec{J}^M(t) = \int d\vec{r} \vec{J}^M(\vec{r}, t),$$

we get what Kubo got,

$$D\chi = \lim_{\epsilon \rightarrow 0} (1/3 V k_B T) \int_0^{\infty} dt \frac{1}{2} \{ \vec{J}^M(t), \vec{J}^M(0) \} > e^{-\epsilon t}, \quad (2.29b)$$

where V is the volume of the system, and we have put in a convergence factor  $e^{-\epsilon t}$ , to be safe just in case convergence at large t should be subtle.

### 2.3 Magnetic Neutron Scattering

So far, we have been doing pretty well. Using simple arguments we have obtained an experimentally relevant correlation function.  $S(k, \omega)$  can, as we said, be measured by neutron scattering. Neutrons possess a magnetic moment which interacts with the magnetization of the medium by the magnetic dipole interaction, and leads to scattering. What one does is shoot into the liquid neutrons which have initial energy  $\epsilon_i$  and momentum  $\vec{p}_i$ . One then looks for scattered neutrons with energy  $\epsilon_f = \epsilon_i - \hbar\omega$  and momentum  $\vec{p}_f = \vec{p}_i - \hbar\vec{k}$ . Obviously, the neutrons have lost (or picked up, depending on the sign of  $\omega$ ) energy and momentum to (from) excitations in the system, namely the collective fluctuations of the magnetization; see fig. 2.2.

### 2.3 Magnetic Neutron Scattering

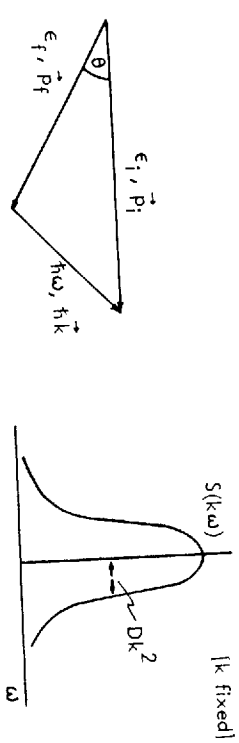


Fig. 2.2

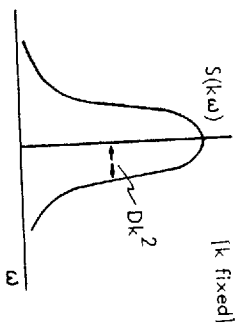


Fig. 2.3

The spectrum of these fluctuations will therefore determine the inelastic scattering cross section. This is shown in the Appendix. For the moment, it will suffice to note that the intensity of the scattered beam,  $I_{scat}$  is given by

$$I_{scat} \begin{pmatrix} \vec{p}_i + \vec{p}_f - \hbar\vec{k} \\ \epsilon_i + \epsilon_f - \hbar\omega \end{pmatrix} = [ \text{factors times} ] S_{MM}(\vec{k}, \omega). \quad (2.30)$$

Eq. (2.25) tells us to expect a Lorentzian line shape for this process, see fig. 2.3. The width of the Lorentzian, at half maximum, is given by  $\Delta k^2$ . Thus, one can measure the spin diffusion coefficient since the [factors] do not involve the frequency shift  $\omega$ . The total area under the Lorentzian,  $\int d\omega S(k, \omega)$ , is given by  $2\pi k_B T \chi$ , and one could also measure the spin susceptibility if the [factors] were accurately known. Unfortunately, absolute intensity measurements are difficult, and the [factors] involve, moreover, magnetic form factors which are often not well known. We also note, finally, that eq. (2.25) holds only for small  $k$  and  $\omega$  which is a region difficult to resolve by neutron scattering. Nevertheless, we meant here to demonstrate the principle of measuring correlation functions by scattering and for this purpose, our example will suffice.

## 2.4 The Static Susceptibility

In this section, eq. (2.23) will be demonstrated, to make good on at least one promise made above. The proof is simple. What we have to show is that

$$\beta^{-1} \chi = \lim_{k \rightarrow 0} \int d\vec{r} e^{-i\vec{k} \cdot \vec{r}} \langle M(\vec{r}) M(0) \rangle_{\text{eq}} \quad (2.31)$$

No time argument is needed here; both operators  $M(\vec{r})$  and  $M(0)$  are taken at  $t = 0$ , i. e., in Schrödinger representation. We can, instead of the dipole moment per unit volume  $M(\vec{r})$ , introduce the total dipole moment operator by

$$M^{\text{tot}} = \int d\vec{r} M(\vec{r}) \equiv MV \quad (2.32)$$

so that we get, using translational invariance,

$$\chi = (\beta/V) \langle M^{\text{tot}} M^{\text{tot}} \rangle_{\text{eq}} \quad (2.33)$$

Now what do we mean by "magnetic susceptibility  $\chi$ "? Phenomenologically, we mean that if we measure the average magnetization (per unit volume)  $\langle M \rangle_h$  in the presence of a constant magnetic field  $h$ , we find  $\langle M \rangle_h = \chi h$  if the external field  $h$  is sufficiently small. (We use  $h$  here rather than the customary  $H$  to avoid confusion with the Hamiltonian.) More precisely,  $\chi$  is experimentally defined by the equation

$$\chi = \left. \frac{\partial \langle M \rangle_h}{\partial h} \right|_{h=0} \quad (2.34)$$

the derivative to be taken at constant volume and temperature. So we have to compute this derivative from statistical mechanics. Now in the presence of a magnetic field  $h$ , the total Hamiltonian is given by

$$\mathcal{H} = H - \int d\vec{r} M(\vec{r}) h = H - M^{\text{tot}} h \quad (2.35)$$

## 2.4 The Static Susceptibility

where  $H$  is the full many-body Hamiltonian of the isolated system. Therefore, the average magnetization is

$$\langle M \rangle_h = \frac{1}{V} \langle M^{\text{tot}} \rangle_h = \frac{1}{V} \frac{\text{tr} e^{-\beta \mathcal{H}} M^{\text{tot}}}{\text{tr} e^{-\beta \mathcal{H}}} = \frac{1}{V} \frac{\text{tr} e^{-\beta [H - M^{\text{tot}} h]} M^{\text{tot}}}{\text{tr} e^{-\beta [H - M^{\text{tot}} h]}} \quad (2.36)$$

in a canonical ensemble. Take the derivative with respect to  $h$  (this can be done painlessly since the operator,  $M^{\text{tot}}$ , is conserved, and thus commutes with  $H$ ) and then set  $h = 0$ . We get

$$\frac{\partial \langle M \rangle_h}{\partial h} \Big|_{h=0} = (\beta/V) \left[ \frac{\text{tr} e^{-\beta H} M^{\text{tot}} M^{\text{tot}}}{\text{tr} e^{-\beta H}} - \left( \frac{\text{tr} e^{-\beta H} M^{\text{tot}}}{\text{tr} e^{-\beta H}} \right)^2 \right]$$

or

$$\chi = (\beta/V) \langle (M^{\text{tot}} - \langle M^{\text{tot}} \rangle_{\text{eq}}) (M^{\text{tot}} - \langle M^{\text{tot}} \rangle_{\text{eq}}) \rangle_{\text{eq}} \quad (2.37)$$

Of course,  $\langle M^{\text{tot}} \rangle_{\text{eq}} = 0$  in the absence of the field  $h$  so that we have derived eq. (2.23) or the equivalent eq. (2.27).

We have written  $\chi$  in the form (2.37) to indicate clearly that the susceptibility is given by the fluctuations of the magnetization from its equilibrium value; static fluctuations, nota bene. This connection should not be too surprising.  $\chi$  measures how easy it is to change the average magnetization by means of an external magnetic field. Clearly, this should be the easier the larger, or more probable, are spontaneous fluctuations of the magnetization from its average value. Similarly, we will see later that the response of the particle density to an increase of the pressure, i. e., the compressibility, is given by the spontaneous fluctuations of the total particle number. And the specific heat, describing the change of the energy with changing temperature, is given by the fluctuations of the energy operator, i. e., by  $\langle H^2 \rangle - \langle H \rangle^2$ . And so on.

Sometimes things are not quite as simple as we have made them. We have calculated the limit  $\lim_{k \rightarrow 0} S(k, t=0)$  by simply setting it equal to  $S(k=0, t=0)$ . Sometimes this is not allowed. For example, for the particle density correlation function at  $t=0$ ,  $S_{nn}(k)$ , the value  $S_{nn}(k=0)$  depends on whether a canonical or grand canonical ensemble is used but the limit  $\lim_{k \rightarrow 0} S_{nn}(k)$  does not. Things also have to be reconsidered when the forces between particles are of long range. For dipole-dipole forces, the measured susceptibility depends on the shape of the sample, for instance. And finally, even if there are only short-ranged forces, there might be long-ranged correlations in some cases which makes the limit as  $k \rightarrow 0$  subtle. We will worry about that when we get to it. In He<sup>3</sup> where we can neglect dipole-dipole forces, and there is no long range order, there are no problems.

### 2.5 Linear Dynamical Response

What we have just calculated can be called the linear thermodynamic or static response to a constant magnetic field. We will now analyze how the system responds dynamically to an external magnetic field  $\delta h^{ext}(\vec{r}, t)$  which varies in space and time in some prescribed fashion. Our reason for doing so is, of course, that this is the way most experiments are performed: You apply an external force of some sort to the system, look what happens, and infer from that the properties of the system itself. Some experiments do not fit this Procrustean bed, of course, but many do, you can't win them all. In particular, in discussing spin diffusion in section 2.1 we assumed that, at  $t=0$ , the system started out from some non-equilibrium state so that  $\langle M(\vec{r}, t) \rangle \neq 0$  initially. Such a non-equilibrium state can be produced, in the laboratory or on paper, by slowly turning on a magnetic field sometime in the distant past, and following the development of the system until  $t=0$  when a  $\langle M(\vec{r}, 0) \rangle \neq 0$  will have resulted. If

### 2.5 Linear Dynamical Response

we then switch off the field, the further time dependence of  $\langle M(\vec{r}, t) \rangle_{\text{non-eq}}$  should coincide with our simple spin diffusion theory if that theory is correct.

Now in an external magnetic field  $\delta h^{ext}(\vec{r}, t)$  the Hamiltonian is explicitly time-dependent, and given by

$$\mathcal{H}(t) = H + \delta h^{ext}(t) = H - \int d\vec{r} \vec{M}(\vec{r}) \delta h^{ext}(\vec{r}, t) \quad (2.38)$$

in Schrödinger representation where the operator  $\vec{M}(\vec{r})$  is time-independent. The time dependence is carried by the density matrix, or ensemble operator,  $\rho(t)$  which describes the state of the system such that the average of  $\vec{M}(\vec{r})$ , or any other operator, at time  $t$  is given by

$$\langle M(\vec{r}, t) \rangle = \text{tr} \rho(t) M(\vec{r}), \quad \text{with } \text{tr} \rho(t) = 1, \quad (2.39)$$

where  $\text{tr}$  is the quantum-mechanical trace.

What follows is entirely parallel to the traditional derivation of the Heisenberg-Kramers formula for the dielectric constant given in elementary quantum mechanics texts. We have to solve the Schrödinger equation for the density matrix,

$$i\hbar \partial_t \rho(t) = [\mathcal{H}(t), \rho(t)] = [H, \rho(t)] + [\delta h^{ext}(t), \rho(t)], \quad (2.40a)$$

subject to the initial condition

$$\rho(t=-\infty) = \rho^0, \quad \text{with } [H, \rho^0] = 0. \quad (2.40b)$$

The initial condition expresses the fact that the system is stationary before  $\delta h^{ext}$  is turned on; we require, of course, that  $\delta h^{ext} \rightarrow 0$  sufficiently rapidly as  $t \rightarrow -\infty$ . For the manipulations, it does not matter what  $\rho^0$  is in detail but it is presumed known. Since the system usually starts out from thermal equilibrium, an appropriate choice for  $\rho^0$  will be a canonical ensemble  $\rho^0 = e^{-\beta H} / \text{tr} e^{-\beta H}$ , with



$N$  fixed, or a grand canonical ensemble  $\rho \sim e^{-\beta(H-\mu N)}$ , or some other stationary state.

Now all we want is the linear (in  $\delta h \text{ ext}$ ) response. But to first order,

(2.40) is easily "solved". Namely,  $\rho(t) = \rho^0 + \delta \rho(t)$  with

$$\delta \rho(t) = \frac{1}{i\hbar} \int_{-\infty}^t dt' e^{-iH(t-t')/\hbar} [\delta h \text{ ext}(t'), \rho^0] e^{iH(t-t')/\hbar}. \quad (2.41)$$

From here, a few simple manipulations will convince you that the induced change in the average magnetization,  $\delta \langle M(\vec{r}, t) \rangle = \text{tr} \rho(t) M(\vec{r}) - \text{tr} \rho^0 M(\vec{r})$ , can be written in the form

$$\delta \langle M(\vec{r}, t) \rangle = \int_{-\infty}^t dt' \int d\vec{r}' \langle \frac{i}{\hbar} [M(\vec{r}, t), M(\vec{r}', t')] \rangle_{\text{eq}} \delta h \text{ ext}(\vec{r}', t') \quad (2.42)$$

where  $[A, B]_{\text{eq}} = AB - BA$  is the commutator, and  $\langle \dots \rangle_{\text{eq}}$  indicates an equilibrium

average,  $\langle A \rangle_{\text{eq}} = \text{tr} \rho^0 A$ . Henceforth, we will drop the subscript "eq". In

(2.42),  $M(\vec{r}, t)$  are the Heisenberg operators for the unperturbed system,

$$M(\vec{r}, t) = e^{iHt/\hbar} M(\vec{r}) e^{-iHt/\hbar}. \quad (2.42a)$$

Eq. (2.42) is the fundamental result of linear response theory. It

shows that the response function is the averaged commutator, rather than the

correlation function  $S(\vec{r}, t)$  as one might have expected. Small matter: the two functions turn out to be essentially equivalent.

It is customary to define the response function by

$$\chi''_{MM}(\vec{r}, t; \vec{r}', t') = \langle \frac{1}{2\hbar} [M(\vec{r}, t), M(\vec{r}', t')] \rangle. \quad (2.43)$$

Since a liquid in equilibrium is translationally invariant in space and time,

$\chi''(\vec{r}, t; \vec{r}', t') = \chi''(\vec{r} - \vec{r}', t - t')$ , and we can define a Fourier transform by

$$\chi''(\vec{r} - \vec{r}', t - t') = \int \frac{d\omega}{2\pi} \int \frac{d\vec{k}}{(2\pi)^3} e^{-i\omega(t-t')} e^{i\vec{k}(\vec{r} - \vec{r}')} \chi''(\vec{k}, \omega). \quad (2.44)$$

Here and henceforth, all frequency integrals extend over the whole real axis:

$\int d\omega \equiv \int_{-\infty}^{\infty} d\omega$ . It is easy to show that  $\chi''(\vec{k}, \omega)$  is real, an odd function of  $\omega$ , and that it only depends on  $k = |\vec{k}|$ , since  $\chi''$  is a commutator of hermitian

operators, and the equilibrium state is invariant under time reversal, parity, and is spatially isotropic. We will also show that  $\text{Im} \chi''(\vec{k}, \omega) \geq 0$  in a stable system.

A useful function is the complex response function  $\chi(k, z)$ , defined by

$$\chi(k, z) = \int \frac{d\omega}{\pi} \frac{\chi''(k, \omega)}{\omega - z}. \quad (2.45)$$

This is an analytic function of the complex frequency variable  $z$  as long as  $\text{Im} z \neq 0$ .

On the real axis it has a branch cut. Of course, if  $z$  is in the upper half plane,  $\chi(k, z)$  is identical with the Laplace transform

$$\chi(k, z) = 2i \int_0^{\infty} dt e^{izt} \chi''(k, t), \quad \text{for } \text{Im} z > 0. \quad (2.46a)$$

On the other hand, if  $z$  is in the lower half plane,  $\chi(k, z)$  is determined from negative times,

$$\chi(k, z) = (-2i) \int_{-\infty}^0 dt e^{izt} \chi''(k, t), \quad \text{for } \text{Im} z < 0. \quad (2.46b)$$

The physical response is given by the limit of  $\chi(k, z)$  as we approach the real frequency axis from above (from the "physical sheet"):

$$\chi(k, \omega) \equiv \lim_{\epsilon \rightarrow 0} \chi(k, \omega + i\epsilon) = \chi'(k, \omega) + i\chi''(k, \omega), \quad (2.47)$$

where

$$\chi'(k, \omega) = P \int \frac{d\omega'}{\pi} \frac{\chi''(k, \omega')}{\omega' - \omega}. \quad (2.47a)$$

$P$  indicates the Cauchy principal value, and  $\omega$  is real.

To demonstrate this statement, and make physical sense out of these definitions, let us go back to eq. (2.42). The response is a convolution in space and time. We decompose  $\delta h \text{ ext}$  and similarly  $\delta \langle M \rangle$  in Fourier amplitudes,

$$\delta h^{\text{ext}}(\vec{r}, t) = \int \frac{d^n k}{(2\pi)^n} \int \frac{d\omega}{2\pi} e^{-i\omega t + i\vec{k}\cdot\vec{r}} \delta h^{\text{ext}}(\vec{k}, \omega), \quad (2.48)$$

and we obtain

$$\delta \langle M \rangle(\vec{k}, \omega) = \chi(\vec{k}, \omega) \delta h^{\text{ext}}(\vec{k}, \omega). \quad (2.49)$$

$\chi(\vec{k}, \omega)$  is therefore the complex dynamical magnetic susceptibility as it is usually defined in electromagnetism. Its imaginary part,  $\chi''(\vec{k}, \omega)$ , must describe absorption, its real part,  $\chi'(\vec{k}, \omega)$ , dispersion just as the standard texts show. Eq. (2.47a) which connects the two, is a Kramers-Kronig relation, expressing causality which is implicit in (2.42). And our as yet unproven positivity statement,  $\omega \chi''(\vec{k}, \omega) \geq 0$ , expresses the fact that a dissipative many-body system takes more energy out of the external field than it gives back.

### 2.6 Hydrodynamics and Correlation Function

We are now in a position to give better than hit-and-run arguments for what we attempted to do in section 2.2--to establish the connection between the hydrodynamic diffusion equation and correlation functions. We approach the matter as we would in the laboratory. First a spatially varying magnetic field  $\delta h(\vec{r})$  is slowly, adiabatically, turned on, to mechanically produce a state with non-zero magnetization. At  $t = 0$ , the field is switched off, and we can follow the relaxation of the induced magnetization as the system returns to equilibrium. Into the general relation (2.42) between force and response, we insert the external field

$$\delta h^{\text{ext}}(\vec{r}, t) = \begin{cases} \delta h(\vec{r}) e^{\epsilon t} & \text{for } t < 0 \\ 0 & \text{for } t > 0 \end{cases} \quad (2.50)$$

At  $t = 0$ , this force has induced the magnetization

### 2.6 Hydrodynamics and Correlation Function

$$\delta \langle M(\vec{r}, t=0) \rangle = 2i \int_0^\infty d\tau \int d\vec{r}' \chi''(\vec{r}-\vec{r}', \tau) e^{-\epsilon\tau} \delta h(\vec{r}'), \quad (2.51a)$$

$$\text{or} \quad \delta \langle M(\vec{k}, t=0) \rangle = \chi(\vec{k}) \delta h(\vec{k}) \quad (2.51b)$$

by spatial Fourier transformation, where

$$\chi(\vec{k}) = \lim_{\epsilon \rightarrow 0} \chi(\vec{k}, z) \Big|_{z=i\epsilon} = \int \frac{d\omega}{2\pi} \chi''(\vec{k}, \omega) / i\epsilon. \quad (2.52)$$

For positive times,  $t > 0$ , (2.42) and (2.50) give

$$\delta \langle M(\vec{r}, t) \rangle = 2i \int_{-\infty}^0 d\tau \int d\vec{r}' \chi''(\vec{r}-\vec{r}', t-\tau) e^{\epsilon\tau} \delta h(\vec{r}'), \quad (2.53a)$$

whose Laplace transform, defined as in (2.8b), is

$$\delta \langle M(\vec{k}, z) \rangle = \int \frac{d\omega}{\pi i} \frac{\chi''(\vec{k}, \omega)}{z(\omega-z)} \delta h(\vec{k}). \quad (2.53b)$$

And if we use (2.51b) to eliminate the external field, we obtain

$$\delta \langle M(\vec{k}, z) \rangle = (1/i z) [\chi(\vec{k}, z) - 1] \delta \langle M(\vec{k}, t=0) \rangle. \quad (2.54)$$

We have inserted the response function (2.45) in an obvious way.

The fundamental result (2.54) is an exact expression. It is, moreover, of the same general form as the hydrodynamic result (2.9), and it describes the same process. Therefore, for small  $\vec{k}$  and  $z$  where hydrodynamics is correct, we can compare (2.54) and (2.9), and obtain

$$\chi(\vec{k}, z) = \frac{i D k^2}{z + i D k^2} \chi(\vec{k}) \quad (2.55a)$$

and in particular, by setting  $z = \omega + i\epsilon$  and taking the imaginary part,

$$\chi''(\vec{k}, \omega) = \frac{D k^2 \omega}{\omega^2 + (D k^2)^2} \chi(\vec{k}). \quad (2.55b)$$

What we have obtained is the correct limiting expression for the magnetic response function. If everything is consistent,  $\chi(k)$  must be the static susceptibility at small  $k$  since then, (2.51b) states that  $[\chi \equiv \chi(k \rightarrow 0)] \delta \epsilon \langle M(\vec{k}) \rangle = \chi \delta h(\vec{k})$  or  $\delta \langle M(\vec{r}) \rangle = \chi \delta h(\vec{r})$  which is how the susceptibility is defined. From (2.52) we can therefore write the thermodynamic sum rule as

$$\chi = \frac{\partial M}{\partial h} \Big|_{h=0} = \lim_{k \rightarrow 0} \int \frac{d\omega}{\pi} \chi''(k, \omega) / \omega. \tag{2.56}$$

And from (2.55b) we find

$$D\chi = \lim_{\omega \rightarrow 0} \lim_{k \rightarrow 0} \left[ \lim_{k \rightarrow 0} \frac{\omega}{k} \chi''(k, \omega) \right], \tag{2.57}$$

which is, again, a Kubo-type relation for the transport coefficient.

Don't miss the point of these results:  $\chi''(k, \omega)$  is, by eqs. (2.43, 44), a mathematically well-defined object. It may not be easy to calculate from a microscopic theory but at least one knows exactly what one should, in principle and in approximation, calculate. And indeed, there are several powerful techniques available for such a calculation. Eqs. (2.56, 57) show how from  $\chi''(k, \omega)$  to obtain the macroscopic parameters  $\chi$  and  $D$ . Undoubtedly, these expressions are now on a much firmer basis than what we have, haphazardly, derived in section 2.2. We shall now show that the respective results are completely equivalent.

2.7 The Fluctuation-Dissipation Theorem

In order to see whether or not we have goofed in section 2.2, i.e., whether or not (2.57) and (2.28) are consistent, for example, we have to establish a connection between the functions  $S(k, \omega)$  and  $\chi''(k, \omega)$ . This connection is given by the celebrated fluctuation-dissipation theorem, discovered by H. Nyquist in 1928 as a relation between noise and dissipation in electric resistors. For our case, this

2.7 The Fluctuation-Dissipation Theorem

theorem (Callen and Welton 1951) states that

$$\chi''(k, \omega) = (1/2\pi)(1 - e^{-\hbar\omega}) S(k, \omega). \tag{2.58}$$

Accepting the theorem for the moment, we see that the Kubo expressions (2.57) and (2.28) are indeed equivalent. With the thermodynamic sum rules (2.56) and (2.27), things are just a little more subtle. If we use (2.58) in (2.56) we get

$$\lim_{k \rightarrow 0} \int \frac{d\omega}{2\pi} \frac{1}{\hbar\omega} (1 - e^{-\hbar\omega\beta}) S(k, \omega) = \chi = \lim_{k \rightarrow 0} \beta \int \frac{d\omega}{2\pi} S(k, \omega). \tag{2.59}$$

After our derivations in sections 2.4-6, we cannot very well doubt either

(2.27) or (2.56). Now notice that if it were true that  $\lim_{k \rightarrow 0} S(k, \omega) \sim \delta(\omega)$  we

would be all set since  $\omega^n \delta(\omega) = 0$  for  $n > 0$ , and therefore  $(1/\hbar\omega)(1 - e^{-\hbar\omega\beta}) \delta(\omega) = \beta \delta(\omega)$  so that the two sides in (2.59) would indeed be identical. Now is

$S(k=0, \omega) \sim \delta(\omega)$ ? Well,

$$S(k=0, \omega) = \int d\vec{r} \langle M(\vec{r}, t) M(0, 0) \rangle = \langle M^{tot}(t) M(0, 0) \rangle \tag{2.60}$$

as in section 2.4. But  $M^{tot}(t)$ , the total dipole moment, is conserved, vide eq. (2.5). Therefore,  $S(k=0, \omega)$  is in fact independent of time, and its Fourier transform

$$S(k=0, \omega) = \text{const} \int_{-\infty}^{\infty} dt e^{i\omega t} = \text{const} 2\pi \delta(\omega). \tag{2.61}$$

So indeed, the  $\omega$  in (2.59) is unnecessary, and the two expressions (2.56) and (2.27) for the susceptibility are completely equivalent. We might note, parenthetically, that if  $M^{tot}$  were not conserved we would have to revisit section 2.4 in fact since we assumed there that  $[M^{tot}, H] = 0$ . No such assumption was implicit in the derivation of (2.56), and in this case, (2.56) is the correct equation as one can also show from (2.36) and (2.58).

Since our derivation of  $\chi''$  in section 2.6 is much more convincing than that of  $S$  in section 2.2, let us use the former to correct the latter. Instead of (2.25), we should have

$$S(k, \omega) = \frac{\hbar \omega \beta}{1 - e^{-\hbar \omega \beta}} \times \frac{Dk^2}{\omega^2 + (Dk^2)^2} \frac{2}{\beta} \chi. \quad (2.62)$$

Thus  $S(k, \omega)$  is not quite symmetric in  $\omega$ . At positive frequency  $\omega > 0$  it is a little stronger than at negative frequency  $\omega < 0$ . Indeed, since  $\omega \chi'(k, \omega)$  is always even in  $\omega$ , it is generally true that

$$S(k, -\omega) = e^{-\hbar \omega \beta} S(k, \omega). \quad (2.63)$$

This result makes eminent sense in the light of what we said above about neutron scattering. According to (2.30),  $\epsilon_f = \epsilon_i - \hbar \omega$ . Positive frequency means the neutron has lost energy to the system (by creating an excitation of energy  $\hbar \omega$ ) while negative frequency describes a process in which the neutron has picked up energy from the system (by destroying an excitation). Of course, to destroy an excitation you must first have one, and their relative abundance is given by  $e^{-\hbar \omega \beta}$ . "Die N urnberger hngen keinen, sie hdtten ihn denn." (Schinderhannes)

The dissymmetry of the scattering intensity,  $\sim S(k, \omega)$ , is only pronounced at low temperatures,  $k_B T \lesssim \hbar \omega$ . It is absent classically. It is an important effect in Raman spectra in solids which probe optical phonons of relatively large energy. For hydrodynamic modes, the frequency is so small that the prefactor in Eq. (2.62) is, effectively, unity.

And now we had better prove (2.58). Since we will use this theorem often, and since its proof is simple, let us consider correlations between the arbitrary observables  $A_i(t)$  and  $A_j(t)$ , defining

## 2.7 The Fluctuation-Dissipation Theorem

$$S_{ij}(t) = \langle A_i(t) A_j(0) \rangle - \langle A_i(t) \rangle \langle A_j(0) \rangle,$$

$$\chi''_{ij}(t) = \langle \frac{1}{2\hbar} [A_i(t), A_j(0)] \rangle.$$

We have subtracted the equilibrium averages in (2.64a) so that  $S_{ij}(t) \rightarrow 0$   $t \rightarrow \infty$ , and thus its Fourier transform  $S_{ij}(\omega)$  presumably exists. Of course  $\langle A_i(t) \rangle$  is independent of time.

Let us perform the average over a canonical ensemble  $\rho = e^{-\beta H}$ . Because the operator,  $e^{-\beta H}$ , effects a time translation by the imaginary  $\tau = i\hbar\beta$ , see (2.42a),

$$\text{tr} e^{-\beta H} A_i(t) A_j(0) = \text{tr} A_i(t + i\hbar\beta) e^{-\beta H} A_j(0)$$

$$= \text{tr} e^{-\beta H} A_i(0) A_j(t + i\hbar\beta),$$

where we have used the cyclic invariance of the trace,  $\text{tr} AB = \text{tr} BA$ . Of time translation invariance,  $\langle A_i(t) A_j(0) \rangle = \langle A_i(0) A_j(-t) \rangle$ , we therefore

$$S_{ij}(-t) = S_{ij}(t - i\hbar\beta) = e^{-\beta \hbar \partial_t} S_{ij}(t).$$

And thus easily from (2.64)

$$2\hbar \chi''_{ij}(t) = S_{ij}(t) - S_{ij}(-t) = \int_0^{\hbar} dt' e^{-\beta \hbar t'} S_{ij}(t + t'),$$

whose Fourier transform,  $\partial_t \rightarrow -i\omega$ , is

$$2\hbar \chi''_{ij}(\omega) = (1 - e^{-\hbar \omega \beta}) S_{ij}(\omega).$$

This is essentially eq. (2.58). We only have to recognize that  $\vec{r}$ , the argument of  $M(\vec{r})$ , is an operator label like  $i$  above. For the magnetization correlation functions we get therefore the equation

$$\chi''_{MM}(t-t') = (1 - e^{-t|w|}) S_{MM}(t-t'), \tag{2.68}$$

whose spatial Fourier transform, eq. (2.58), we set out to prove. We will have more comments about this theorem in the next chapter.

2.8 Positivity of  $w\chi''(kw)$

We pointed out after eq. (2.44) that

$$w\chi''(kw) \geq 0 \text{ for all } k \text{ and } w. \tag{2.69}$$

The significance of this property is already clear from the foregoing. From (2.56) we see that it implies that the spin magnetic susceptibility  $\chi$  is positive which is a necessary condition for the thermodynamic stability of the system. From (2.57) we see that it also implies that the spin diffusion coefficient  $D$  is positive which is necessary for the system to be dynamically stable, see eq. (2.10). And finally, since (2.69) is tantamount, because of the fluctuation dissipation theorem, to the assertion that  $S(kw) \geq 0$ , it is necessary for the interpretation of the function  $S(kw)$  as a spectral density of fluctuations.

(2.69) is quickly proved. We take again an arbitrary set  $\{A_i(t)\}$  of observables, and consider  $S_{ii}(t, t')$  in the form

$$S_{ii}(t, t') = \langle (A_i(t) - \langle A_i(t) \rangle)(A_i(t') - \langle A_i(t') \rangle) \rangle. \tag{2.70}$$

Multiplying with any set of functions  $q_i(t)$  and integrating over some large time  $T$ ,

we obtain

$$\sum_{i,j} (2T)^{-1} \int_{-T}^T dt \int_{-T}^T dt' q_i^*(t) S_{ij}(t, t') q_j(t') = \langle A^* A \rangle \geq 0, \tag{2.71}$$

where

$$A = \sum_i (2T)^{-1/2} \int_{-T}^T dt [A_i(t) - \langle A_i(t) \rangle] \sigma_i(t). \tag{2.71a}$$

If we choose, in particular,  $q_i(t) = \sigma_i e^{-i\omega t}$  and remember that  $S_{ii}(t, t') = S_{ii}(t-t')$ , then in the limit of large  $T$  we find

$$\langle A^* A \rangle = \sum_{i,j} q_i^* S_{ij}(\omega) q_j \geq 0 \tag{2.72a}$$

which is equivalent, because of (2.67b), to

$$\sum_{i,j} q_i^* w\chi''_{ij}(w) q_j \geq 0. \tag{2.72b}$$

Again, the operator label  $i$  will, in cases considered here, include the continuous variable  $\vec{r}$ , and  $\sum_i$  is replaced by  $\int d\vec{r}$ . The choice  $q_i = \sigma(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}$  and translational invariance in space yields

$$S_{MM}(kw) \geq 0 \text{ or } w\chi''_{MM}(kw) \geq 0. \tag{2.73}$$

This demonstration is, of course, a bit relaxed. It can be fancied up considerably, but too much mathematical rigor may not be in place when one deals with  $10^{23}$  particles. A more physical dynamical proof, which elucidates the fundamental connection between (2.73) and the dissipative property of many-particle systems, is given in section 3.3.

2.9 Sum Rules

From (2.43) one sees that

$$\left( i \frac{\partial}{\partial t} \right)^n \chi''(\vec{r}, t, t') = \frac{1}{2\pi} \left[ \left( i \frac{\partial}{\partial \vec{r}} \right)^n M(\vec{r}, t), M(\vec{r}', t') \right]. \tag{2.74}$$

Taken at equal times  $t = t'$ , this means that

$$\int \frac{d\omega}{\pi} w^n \chi''(kw) = \int d(\vec{r}-\vec{r}') e^{-i\vec{k}\cdot(\vec{r}-\vec{r}')} \frac{1}{2\pi} \left[ \left( i \frac{\partial}{\partial \vec{r}} \right)^n M(\vec{r}, t), M(\vec{r}', t) \right], \tag{2.75}$$

where

$$i^n M(\vec{r}, t) \equiv (i \frac{\partial}{\partial t})^n M(\vec{r}, t) = \left(\frac{1}{\hbar}\right)^n [\dots [M(\vec{r}, t), H], \dots, H]. \quad (2.75a)$$

Thus the right hand side of (2.75) contains a sequence of equal time commutators which can in principle, and in some cases in fact, be exactly calculated. The simplest of these is the sum rule for  $n = 1$ . (Clearly, since  $\chi''(k; \omega)$  is an odd function of  $\omega$  all sum rules for even  $n$  vanish.) Namely,

$$i \frac{\partial}{\partial t} \chi''(\vec{r}-\vec{r}', t-t') = \frac{-i}{2\hbar} \nabla' \cdot \langle [i^2 M(\vec{r}, t), M(\vec{r}', t')] \rangle \quad (2.76)$$

because of the conservation law (2.3). At equal times, the commutator is easily evaluated. From the explicit expressions for the magnetization operator and its current, Eqs. (2.2, 4), one finds

$$[i^2 M(\vec{r}, t), M(\vec{r}', t')] = \frac{\mu^2}{m} i \hbar \nabla' \cdot [n(\vec{r}) \delta(\vec{r}-\vec{r}')] \quad (2.77)$$

which is "a very disguised version of the fundamental statement that the commutator of the position and the momentum is  $i\hbar$ ".  $n(\vec{r}) = \sum_{\alpha} \delta(\vec{r}-\vec{r}_{\alpha})$  is the particle density (operator). Thus we find the sum rule

$$\int \frac{d\omega}{\pi} \omega \chi''(k; \omega) = \frac{\mu^2}{m} k^2. \quad (2.78)$$

This is the spin analog of the famous f-sum rule. By contrast to the thermodynamic sum rule which we found earlier, eq. (2.56), and which holds only as  $k \rightarrow 0$ , (2.78) is exact for all  $k$ . Further sum rules can be derived, but with rapidly increasing labor.

The sum rules provide the coefficients for an expansion of  $\chi(k; z)$  for large  $z$ . From its definition in (2.45), we see that for large  $z$

$$\chi(k; z) = -\sum_{n=1}^{\infty} \frac{\langle i^n M(k) \rangle}{z^n} \chi(k), \quad (2.79a)$$

where

## 2.10 Relaxation Time Approximation

$$\langle i^n M(k) \rangle = \frac{\int \frac{d\omega}{\pi} \omega^n \chi''(k; \omega) / \omega}{\int \frac{d\omega}{\pi} \chi''(k; \omega) / \omega}.$$

From its derivation which expands  $[1-x/z]^n = 1 + (n/x)z + \dots$  clear that this expansion can only be asymptotic. It is valid when  $|z|$  compared to all frequencies in the system" which means, all frequencies which  $\chi''(k; \omega)$  is not effectively zero.

We can also relate the sum rules to a Taylor expansion in  $z$  should be apparent from (2.74, 75). (2.79) is equivalent to

$$\chi''(k, t) = \frac{1}{z} \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} \langle i^{n+1} M(k) \rangle \chi(k),$$

which makes it clear that the high-frequency expansion is equivalent to time expansion.

### 2.10 Relaxation Time Approximation

An interesting feature of the sum rules is their very existence no reason why the thermodynamic average of the multiple commutators should not exist, for all  $n$ , and in many cases this can in fact be rigorous. This means, then, that  $\chi''(k; \omega)$  has to fall off sufficiently rapidly at large  $\omega$  all of its moments are finite.

Evidently, the hydrodynamic approximation for  $\chi''(k; \omega)$ , eq. (2.56) does not have this property. Indeed, while it exhausts the "thermodynamic rule (2.56), it fails to satisfy even the first high-frequency sum rule (2.78). Lorentzian dies off too slowly in the wings.

This situation can be remedied in a simple fashion. Since, so explicit expression (2.55b) for  $\chi''$  is not much more than a fancy way of diffusion equation, let us now try to improve the theory by improving the

phenomenological equation which it represents.

The constitutive equation

$$\langle \vec{I}^M(\vec{r}, t) \rangle = -D \vec{\nabla} \langle M(\vec{r}, t) \rangle \quad (2.6)$$

from which we started, implies that the current follows changes in the magnetization instantaneously. This is true when  $\langle M \rangle$  varies extremely slowly in time, i. e., for small frequencies. However, when  $\langle M(\vec{r}, t) \rangle$  varies more rapidly, i. e., for larger frequencies, the current cannot keep up, and there must be a time lag between  $M$  and  $\vec{I}^M$ . Instead of (2.6), let us therefore try

$$\langle \vec{I}^M(\vec{r}, t) \rangle = -\int_0^t dt' D(t-t') \vec{\nabla} \langle M(\vec{r}, t') \rangle. \quad (2.81)$$

This equation incorporates causality: the current must follow the magnetization fluctuation which causes it. We have fixed the lower limit at  $t = 0$  since for negative times, when the initial disturbance is adiabatically created, the current surely vanishes. Indeed, it is a good exercise to prove that the  $f$ -sum rule cannot be satisfied as long as  $\langle I^M \rangle \neq 0$  at  $t = 0$ . That is what is wrong with eq. (2.6).

The function  $D(t-t')$ , appropriately called a memory function, incorporates all the complicated rapid processes which are set in motion by the initial disturbance. Let us assume, for simplicity, that all these processes can be described by a single relaxation time  $\tau$ , i. e., that

$$D(t-t') = (D/\tau) e^{-(t-t')/\tau}. \quad (2.82)$$

Putting it all into the continuity equation (2.3), we solve as before:

$$\langle M(\vec{k}, z) \rangle = \frac{i}{z + ik^2 D/(1-iz\tau)} \langle M(\vec{k}, t=0) \rangle. \quad (2.83a)$$

And just as before, we obtain from this the response function

$$\chi(k, z) = \frac{ik^2 D/(1-iz\tau)}{z + ik^2 D/(1-iz\tau)} \chi \quad (2.83b)$$

and its absorptive part

$$\chi''(k, \omega) = \frac{\omega k^2 D}{\omega^2 + D^2(k^2 - \omega^2/\tau/D)^2} \chi. \quad (2.83c)$$

Note that with  $D(t-t')$  given by (2.82), the current can be obtained from

$$(\tau \partial_t + 1) \langle \vec{I}^M(\vec{r}, t) \rangle = -D \vec{\nabla} \langle M(\vec{r}, t) \rangle, \quad (2.84a)$$

so that eqs. (2.83) are equivalent to the phenomenological equation of motion

$$[\partial_t^2 + (1/\tau)(\partial_t - D\nabla^2)] \langle M(\vec{r}, t) \rangle = 0. \quad (2.84b)$$

The last few equations are the direct analog of the description employed by Drude and Maxwell for the dielectric response.

What have we gained? For small frequencies,  $(\omega/Dk^2)_{k\tau} \ll 1$ ,

(2.83c) is our old Lorentzian of the hydrodynamic theory. However,  $\chi''(k, \omega)$  now falls off faster in the wings, and sufficiently fast that the first moment is finite:

$$\langle \omega \rangle^{(2)}(k) = \chi^{-1} \int_{-\infty}^{\infty} \frac{d\omega}{\pi} \omega \chi''(k, \omega) = k^2 D/\tau. \quad (2.85)$$

Eqs. (2.83) will therefore give an interpolation formula which is correct at both long and short times, or small and large frequencies. To this end, we require that the exact  $f$ -sum rule (2.78) be fulfilled, and we obtain an expression for the spin diffusion coefficient, namely

$$D = \frac{n\mu^2}{m\chi} \tau. \quad (2.86)$$

Thus we have done our first sum rule calculation. (For similar ideas,

see de Gennes 1959, Mori and Kawasaki 1962, Bennett and Martin 1965.) As a

calculation of  $D$ , it seems barely worth the effort at first since it just replaces one parameter,  $D$ , by another,  $\tau$ . However,  $\tau$  is much more closely related to the microscopic dynamics. It is clearly of the nature of a microscopic collision time, and its numerical value can be estimated from atomic collision cross sections in a gas, for example, or even more crudely, in a classical liquid, assessed to be roughly given by  $\tau_c$  of eq. (2.11). Semiquantitatively, (2.86) is a very useful result.

In He<sup>3</sup> which is a degenerate Fermi liquid at low temperatures, scattering is sharply reduced because of the Pauli principle, and  $\tau \sim 1/T^2$ . The spin susceptibility reduces to the well-known Pauli susceptibility, and is independent of temperature. We therefore expect from eq. (2.86) that  $D \sim T^{-2}$  at low temperatures (Martin 1968), and this is experimentally verified.

Eq. (2.86) also makes an interesting prediction about the behavior of the diffusion constant near a critical point, say in a Heisenberg paramagnet to which our considerations apply with no essential change. As the ferromagnetic transition is approached, the spin susceptibility  $\chi(T)$  increases without bound while there is no reason to expect that the microscopic decay time  $\tau$  is much affected. We therefore expect that the diffusion constant goes to zero. This critical slowing down (see eq. (2.10)) is a general phenomenon. It is coupled as eq. (2.83c) shows, with a tremendous increase in the amplitude of spontaneous fluctuations which leads to strong scattering. Near the liquid-gas transition in normal fluids, this accounts for the entirely analogous phenomenon of critical opalescence (for critical phenomena, see Stanley 1971).

While the result for  $\chi''(k, \omega)$  is somewhat improved from eqs. (2.55) to (2.83), all higher frequency moments  $\langle \chi''(k) \rangle$ ,  $n \geq 4$ , still diverge. This can now be easily remedied. Remember that the relaxation time ansatz (2.82) was quite ad hoc. For arbitrary memory  $D(t)$ , we would obtain

## 2.10 Relaxation Time Approximation

$$\chi(k, z) = \frac{ik^2 D(z)}{z + ik^2 D(z)} \chi, \quad (2.84)$$

which makes it plain that what the "constitutive equation with memory" does is introduce frequency dependence into the transport coefficient

$$D(z) = \int_0^{\infty} e^{-izt} D(t) dt = \frac{\int_0^{\infty} dt e^{-izt} D'(t)}{z - z} \quad (Imz > 0), \quad (2.85)$$

where  $D(t)$  and  $D'(t) = \int_{-\infty}^{\infty} dt e^{i\omega t} D(t)$  can always be chosen as real functions of their argument. Also

$$\chi''(k, \omega) = \frac{\omega k^2 D'(\omega)/2}{[\gamma^2 + k^2 P \int_{-\infty}^{\infty} \frac{d\omega'}{2\pi} \frac{D'(\omega')}{\omega' - \omega}]^2 + [k^2 D'(\omega)/2]^2} \quad (2.86)$$

The function  $D'(t)$  must therefore be positive.

From (2.87c) or more easily from (2.87a) it is easy to see  $n$  moments of  $\chi''(k, \omega)$  will be finite if we choose a  $D'(t)$  whose first  $n$  moments are finite. In particular, the  $f$ -sum rule is fulfilled if

$$\int_{-\infty}^{\infty} \frac{d\omega}{\pi} \omega^n \chi''(k, \omega) = k^2 \int_{-\infty}^{\infty} \frac{d\omega'}{\pi} \omega'^n D'(t) \quad (2.87a)$$

or

$$D'(t=0) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} D'(t) = \frac{\eta \mu^2}{m \chi} \quad (2.87b)$$

All this sum rule does, therefore, is to prescribe the value of the memory function  $D(t)$  at  $t=0$ . This may be a helpful reminder for the occasional reader who is overly impressed by these general results. The complexity of a memory function does not disappear quite so easily. Since it leads to finite order, one often prefers a Gaussian memory

$$D(t) = \frac{\eta \mu^2}{m \chi} e^{-\pi(t/2\tau)^2} \quad \text{or} \quad D'(t) = \frac{\eta \mu^2}{m \chi} (2\tau)^{-2} e^{-(i\omega\tau)^2/\pi} \quad (2.88)$$



but many other functions are equally good candidates. (The Gaussian has also some appeal for stochastic reasons.)

For hydrodynamically long times, one probes only the integrated effect of the rapid processes contained in  $D(t)$ . For any  $D(t)$ , the hydrodynamic diffusion coefficient is given by

$$D = \lim_{z \rightarrow 0} D(z) = \int_0^{\infty} dt D(t) = \frac{1}{z} \lim_{\omega \rightarrow 0} D'(\omega) \quad (2.90)$$

which follows, for example, from (2.87c) and the Kubo relation (2.57). This also gives a more precise meaning to the relaxation time of eq. (2.86).  $\tau$  is the average "memory time",

$$\tau = [1/D(\tau = 0)] \int_0^{\infty} dt D(t) . \quad (2.91)$$

There is one simple fact about the time dependence of  $D(t)$  which we know for certain, namely that

$$|D(t)| \leq D(t = 0), \quad (2.92)$$

which is a simple consequence of  $D'(\omega) \geq 0$ . Loss of memory as time passes, is a general phenomenon in nature.

### 2.11 Dispersion Relation Representation

We have said almost everything that can be said without doing more detailed microscopic calculations. However, the linear constitutive relation (2.81) can be generalized a little further. We have first relaxed (2.6) to allow for memory effects. If we in addition allow for a spatially non-local connection between current and magnetization (or gradient of the latter, rather, a spatially constant magnetization will evidently not give rise to a current) we obtain

### 2.11 Dispersion Relation Representation

$$\langle \vec{r}^M(\vec{r}, t) \rangle = - \int_0^t dt' \int d\vec{r}' D(\vec{r} - \vec{r}', t - t') \vec{\nabla}' \cdot \langle M(\vec{r}', t') \rangle . \quad (2.93)$$

This leads to

$$\chi(k, z) = \frac{ik^2 D(k, z)}{z + ik^2 D(k, z)} \chi(k), \quad (2.94)$$

where

$$D'(k, \omega) = \int_{-\infty}^{\infty} dt \int d\vec{r} e^{i\vec{r} \cdot \vec{k} - i\omega t} D(\vec{r}, t), \quad (2.95a)$$

$$D(k, z) = \int \frac{d\omega}{2\pi} \frac{D'(k, \omega)}{\omega - z} . \quad (2.95b)$$

$D'(k, \omega)$  can again be chosen real, even in  $\omega$ , and a function of  $|\vec{k}|$  only. Its Hilbert transform,  $D(k, z)$ , is closely related to what, in field theory, would be called the self-energy. From (2.94),  $\chi''(k, \omega)$  is given by

$$\chi''(k, \omega) = \frac{ik^2 D'(k, \omega)/2}{\left[ \int \frac{d\omega'}{2\pi} k^2 \frac{D'(k, \omega')}{\omega' - \omega} \right] + [k^2 D'(k, \omega)/2]} . \quad (2.96)$$

We will now show that these formulae, which replace the hydrodynamic transport coefficient by a  $k$ - and  $z$ -dependent object, are in fact completely general. Of course, since (2.94) simply defines the function  $D(k, z)$  in terms of  $\chi(k, z)$  by

$$D(k, z) = \frac{iz}{k^2} \left[ 1 - \frac{\chi(k)}{\chi(k, z)} \right]^{-1} = \frac{\chi(k, z)/k^2}{(1/iz) [\chi(k, z) - \chi(k)]} , \quad (2.97)$$

the only thing that has to be proved is that this expression is indeed an analytic function of  $z$ , for  $\text{Im} z \neq 0$ , as implied by the representation (2.95b). Now we know that  $\chi(k, z)$  is analytic everywhere, except on the real axis, of course. All that could go wrong, therefore, is that the denominator,

$$\frac{1}{z} [X(kz) - X(k)] = \int_{\pi}^{\pi} \frac{du}{\pi} \frac{X''(ku)}{u(u-z)} = 0, \tag{2.98}$$

would vanish for some  $z$  off the real axis. However, for  $z = x + iy$

$$\text{Re} \int_{\pi}^{\pi} \frac{du}{\pi} \frac{X''(ku)}{u(u-z)} = \int_{\pi}^{\pi} \frac{du}{\pi} \frac{y}{(u-x)^2 + y^2} \frac{X''(ku)}{u} \neq 0 \text{ if } y \neq 0 \tag{2.99}$$

cannot vanish anywhere ( $y \neq 0$ ) since  $X''(kx)/u$  is non-negative, and thus (2.98) cannot vanish for  $\text{Im}z \neq 0$ . Hence,  $D(kz)$  as defined by (2.94, 97) is analytic, and (2.95b) is a proper representation.

There is a point to being suspicious of exact results of complete generality when they pertain to a complicated many-body system. If they are so general, how can they be practically useful? What we have proved is an exact dispersion relation (2.96) for  $X''(kx)$ . That is not awfully much since it just introduces another unknown function  $D'(ku)$  to describe  $X''(kx)$ . And indeed, many different kinds of dispersion relations can easily be proved (Kadonoff and Martin 1963). What makes the present one nonetheless valuable is that in the important region of small  $k$  and  $x$  where  $X''(kx)$  has a complicated analytic structure,  $D'(ku)$  is presumably well-behaved, with its value at  $k=0$  and  $x=0$  given by

$$\frac{1}{2} D'(0,0) = D, \tag{2.100}$$

the spin diffusion coefficient. Thus, for small  $k$  and  $w$ ,  $D'(kw)$  is a simpler object than  $X''(kw)$ , and approximations to  $D'(kw)$  have a better chance of success. All of our previous results, such as (2.55b) or (2.83c), represent such approximations.

It is instructive to recover the hydrodynamic result (2.55) from the

### 2.11 Dispersion Relation Representation

general representation (2.94). This equation, or equivalently

$$\frac{1}{z\beta} [X(kz) - X(k)] \equiv C(kz) = \frac{1}{z + ik^2 D(kz)} i\beta^{-1} X(k),$$

does incorporate one important feature of the dynamics: the constant  $C(kz)$  is the origin of the factor  $k^2$  in (2.101), and thus at  $k=0$ ,  $C(kz)$  is finite. As  $k$  becomes finite, the pole migrates into the lower half plane at  $z = z^0(k)$  which is the solution of

$$z^0 + ik^2 D(k, z^0) = 0.$$

Note that in (2.102)  $D(kz)$  is not the function (2.95b) for  $\text{Im}z < 0$  that function, analytically continued from the upper half  $z$ -plane branch cut on the real axis, onto a second Riemann sheet. For a solution  $z^0(k)$  of (2.102), we can expand the slowly varying function  $D(k, z)$  to first order

$$z + ik^2 D(kz) = (z - z^0(k)) Z^{-1}(k),$$

where

$$Z^{-1}(k) = 1 + ik^2 \frac{\partial D(kz)}{\partial z} \Big|_{z=z^0(k)}.$$

Near  $z^0(k)$  therefore

$$C(kz) = \frac{Z(k)}{z - z^0(k)} i\beta^{-1} X(k).$$

The constant  $Z(k)$  is the pole strength, akin to the wave function constant in field theory. And to order  $k^2$ ,

$$z^0(k) = ik^2 D(0,0) \text{ and } Z(k) = 1,$$

which is the hydrodynamic result, and gives precise meaning to result, eq. (2.55), is a rigorous asymptotic expression for the

Let us, finally, mention one more approximation which is, by contrast, a high-frequency or short-time approximation. It is obtained by replacing  $D(k, t)$  by its value at  $t = 0$ ,  $D(k)$ . Alternatively, we might say that we replace  $D(k, t)$  by the first term in its high-frequency expansion,  $D(k, z) = (i/z)D(k) + D(z^{-3})$ .

The constant  $D(k)$  is again determined by the  $f$ -sum rule, and given by

$$D(k) = \int_{-\infty}^{\infty} dt D'(k, t) = \chi^{-1}(k) k^{-2} \int_{-\infty}^{\infty} dt \langle \chi^{\dagger}(k, t) \chi(k, 0) \rangle = \frac{\eta \mu^2}{m \chi(k)}, \quad (2.106)$$

so that  $D(k)$  is real and positive. If we put this into (2.94) we obtain

$$\chi(k, z) = \frac{-k^2 D(k)}{z^2 - k^2 D(k)} \chi(k), \quad (2.107)$$

At high frequency therefore where this approximation is valid, we find reactive, rather than diffusive, behavior. There is a sound-like mode, with a propagation velocity at small  $k$  which is given by

$$\omega = ck; \quad c^2 = \lim_{k \rightarrow 0} \frac{\langle \chi^{\dagger}(k) \chi(k) \rangle}{k^2} = \frac{\eta \mu^2}{m \chi}. \quad (2.108)$$

This feature, reactive behavior at high frequencies, is a very general phenomenon. For a second example, a normal liquid like water is viscous at low frequency; it exerts no resistance to slowly varying shear forces. If you dive into the ocean softly, it will do you no harm. At high frequencies, however, the liquid becomes elastic: if you fall into the sea from a high-flying plane your last impression might be that the water must have been frozen.

This concludes, for the moment, what we have to say about our simple example---spin diffusion. Clearly, most of what we said applies to other diffusion processes as well. At least for the spectrum at low frequency and wave vector, the main input, really, was the fact that the magnetization is conserved. Our considerations apply literally to the isotropic Heisenberg paramagnet (Bennett and Martin 1965) which can also be described by the simple diffusion equation.

(For large wavelength, the lattice structure does not matter.) Of course, while in the liquid case treated here, diffusion comes about because the spins are carried along by the atoms in the liquid, in the Heisenberg paramagnet the atoms stay put on fixed lattice sites. The diffusion of magnetization takes place via spin-flip interaction between neighbors.

An occasional reader might be concerned about the fact that we have treated the magnetization as a scalar quantity.  $\vec{M}(\vec{r}, t)$  is a (pseudo-)vector of course, and  $I_i^M$  a tensor. However, the vector character of  $\vec{M}$  is quite irrelevant. The point is that the Hamiltonian  $H$  is separately invariant under rotations in spin space. Because of this property, which is intimately related to the existence of the conservation law (2.5), of course, one can treat  $\vec{M}(\vec{r}, t)$  which is a vector in spin space, as a scalar in real space. If you wish, you can take  $M_x$  and  $I_x^M$  everywhere; the  $y$ - and  $z$ -components obey precisely the same equations, with the same diffusion constant  $D$  etc.

Many other processes fit our description as well. An example is the Brownian motion of a heavy particle immersed in a fluid of light particles. In chapter 6, we will consider this process in a slightly different formulation. In this case, the mass ratio  $m/M$  plays the role of the wave vector  $k$  above.

Transverse momentum transport in a normal fluid also follows a hydrodynamic diffusion law, and everything we said above applies, mutatis mutandis, to this process, too. However, the longitudinal behavior which has to do with compressions and temperature fluctuations, is complicated by the fact that several hydrodynamic modes are coupled. Another, and entirely new, aspect has to be considered in systems such as the Heisenberg ferromagnet, superfluid helium, or liquid crystals. These are ordered systems, and we will have to discuss how the presence of order affects the mode structure.

## 3.1 Linear Dynamical Response

We are now interested in the dynamics of several observables

$\{A_i(\vec{r}, t)\}$ . If each of those couples to a small external field  $\delta a_i^{\text{ext}}(\vec{r}, t)$ ,

Hamiltonian in the presence of these fields is given by

$$\mathcal{H}(t) = H - \sum_i \int d\vec{r} A_i(\vec{r}) \delta a_i^{\text{ext}}(\vec{r}, t)$$

in Schrödinger representation. As in section 2.5 we calculate by time-

perturbation theory the linear response. That is, we want to know the ind-

value of  $\langle B(\vec{r}, t) \rangle_{\text{non-eq.}} = \langle B(\vec{r}, t) \rangle_{\text{eq.}} + \delta \langle B(\vec{r}, t) \rangle$  for some variable  $B(\vec{r}, t)$

we start out from equilibrium at  $t = -\infty$ , and let the system evolve under

Proceeding exactly as in section 2.5, we obtain

$$\delta \langle B(\vec{r}, t) \rangle = \sum_{i=-\infty}^t \int_{i=-\infty}^t dt' \int d\vec{r}' \left\langle \frac{i}{\hbar} [B(\vec{r}, t), A_i(\vec{r}', t')] \right\rangle \delta a_i^{\text{ext}}(\vec{r}', t')$$

In particular, the induced change in the variable  $A_i$  from its equilibrium

$$\delta \langle A_i(\vec{r}, t) \rangle = \sum_{i=-\infty}^t \int_{i=-\infty}^t dt' \int d\vec{r}' [2i \chi_{ii}^{\text{ret}}(\vec{r}t, \vec{r}'t') \delta a_i^{\text{ext}}(\vec{r}', t')],$$

where the response function is now a matrix, and given by

$$\chi_{ii}^{\text{ret}}(\vec{r}t, \vec{r}'t') = \chi_{ii}^{\text{ret}}(\vec{r}-\vec{r}', t-t') = \left\langle \frac{1}{2\hbar} [A_i(\vec{r}, t), A_i(\vec{r}', t')] \right\rangle,$$

in a translationally invariant system. If we define its Fourier transform as

$$\chi_{ii}^{\text{ret}}(\vec{k}\omega) = \int_{-\infty}^{\infty} dt(t-t') \int d(\vec{r}-\vec{r}') e^{i\omega(t-t') - i\vec{k} \cdot (\vec{r}-\vec{r}')} \chi_{ii}^{\text{ret}}(\vec{r}t, \vec{r}'t')$$

and the matrix of response functions by

$$\chi_{-i}(kz) = \int \frac{dz}{\pi} \frac{\chi_{ii}^{\text{ret}}(k\omega)}{\omega - z} \quad (\text{Im}z \neq 0),$$

then we can write (3.3) in the form

$$\delta \langle A_i \rangle(k\omega) = \chi_{-i}(k\omega) \delta a_i^{\text{ext}}(k\omega),$$

## CHAPTER 3

## FORMAL PROPERTIES OF CORRELATION FUNCTIONS

The purpose of this chapter is chiefly to summarize the formal results

obtained so far, and extend them to the important case where we are interested

in the correlations among several physical quantities. In the simple example of

spin diffusion, we were only concerned with the "autocorrelation function"

$S_{MM}(\vec{r}t, \vec{r}'t')$  of the magnetization, the probability essentially of finding the magnetization at the space-time point  $\vec{r}, t$  if you know its value at the point

$\vec{r}', t'$ . Now in a liquid, there are several quantities of interest: the particle

density  $n(\vec{r}, t)$ , the momentum density  $\vec{g}(\vec{r}, t)$ , the energy density  $\epsilon(\vec{r}, t)$ , and may-

be others. And these are dynamically coupled. A local imbalance in the energy

density (i.e., a temperature inhomogeneity) will result in a spatially varying

particle density as well, for example. We are therefore led to consider such

correlation functions as  $S_{ne}(\vec{r}t, \vec{r}'t') = \langle [n(\vec{r}t) e(\vec{r}'t')] - \langle n(\vec{r}t) \rangle \langle e(\vec{r}'t') \rangle \rangle$ .

Or else, since we found that the averaged commutator was a little closer to the action, such response functions as  $\chi_{ne}^{\text{ret}}(\vec{r}t, \vec{r}'t') = \langle \langle (1/2\hbar) [n(\vec{r}t), e(\vec{r}'t')] \rangle \rangle$ . We

will therefore consider the general properties of multivariate correlation functions,

most of which are obtained by a perfectly straightforward extension from the case

of a single variable. We shall treat the general, quantum-mechanical, case

which is formally a little easier to handle in fact, and indicate classical limits

where appropriate. This chapter follows in much detail Martin 1968; see also

Berne and Harp 1970.

where

$$\begin{aligned} \chi_{ij}(\vec{k}, \omega) &\equiv \lim_{\epsilon \rightarrow 0} \chi_{ij}(\vec{k}, z) \Big|_{z=i\omega+\epsilon} \\ &= P \int \frac{d\omega'}{\pi} \frac{\chi_{ij}''(\vec{k}, \omega')}{\omega' - \omega} + i \chi_{ij}''(\vec{k}, \omega), \end{aligned} \quad (3.7c)$$

and where, here and henceforth, summation over repeated indices is implied. These equations are perfectly analogous to those in section 2.5. Note one minor difference:  $\chi_{ij}''(\vec{k}, \omega)$  need not necessarily be real, for  $i \neq j$ . However,  $\chi_{ii}''(\vec{k}, \omega)$  is always real.

Eq. (3.7) is valid for arbitrary external fields; it identifies  $\chi_{ij}(\vec{k}, z)$  as a matrix of dynamical susceptibilities. Now in particular, we again turn on the external fields slowly, (adiabatically), and we switch them off for positive times:

$$\delta\alpha_i^{\text{ext}}(\vec{r}, t) = \begin{cases} \delta\alpha_i(\vec{r}) e^{i t} & \text{for } t \leq 0, \\ 0 & \text{for } t > 0. \end{cases} \quad (3.8)$$

At  $t = 0$ , such a field (rather, set of fields) will have produced spatially varying values  $\delta \langle A_i(\vec{r}, t = 0) \rangle$  whose spatial Fourier transforms are, from (3.3), given by

$$\delta \langle A_i(\vec{k}, t = 0) \rangle = \chi_{ij}(\vec{k}) \delta\alpha_j(\vec{k}), \quad (\sum_j \text{implied}) \quad (3.9)$$

where

$$\chi_{ij}(\vec{k}) \equiv \int \frac{d\omega}{\pi} \frac{\chi_{ij}''(\vec{k}, \omega)}{\omega}. \quad (3.10)$$

In the limit in which  $\delta\alpha(\vec{r})$  varies slowly in space, i. e., at small  $\vec{k}$ ,  $\chi_{ij}(\vec{k} \rightarrow 0)$  will again reduce to a set of static susceptibilities, or thermodynamic derivatives.

For example, we will find that

$$\lim_{\vec{k} \rightarrow 0} \int \frac{d\omega}{\pi} \frac{\chi_{An}''(\vec{k}, \omega)}{\omega} = \frac{\partial A}{\partial \mu} \Big|_T = n \frac{\partial A}{\partial \rho} \Big|_T. \quad (3.11)$$

But that is hurrying matters a bit.

For  $t > 0$ , the system starts out from the non-equilibrium values (3.9), and left to itself it will relax back towards equilibrium. If we define

$$\delta \langle A_i \rangle(\vec{k}, z) = \int_0^\infty dt e^{-izt} \delta \langle A_i(\vec{k}, t) \rangle, \quad (3.12)$$

then from (3.3) and (3.8) we get

$$\delta \langle A_i \rangle(\vec{k}, z) = \int \frac{d\omega}{\pi} \frac{\chi_{ij}''(\vec{k}, \omega)}{i\omega(\omega - z)} \cdot \delta\alpha_j(\vec{k}), \quad (3.13)$$

or, using the definitions above and the static result (3.9), we get the fundamental result

$$\delta \langle A_i \rangle(\vec{k}, z) = \frac{1}{iz} [ \chi(\vec{k}, z) \chi^{-1}(\vec{k}) - 1 ]_{ij} \delta \langle A_j(\vec{k}, t = 0) \rangle, \quad (3.14)$$

which is to be read as a matrix equation. We will see that the matrix  $\chi(\vec{k})$  is positive so that its inverse always exists.

Note the advantage of (3.14) over (3.13). The external fields  $\delta\alpha_i$ , whose physical realization may sometimes be hard to assess, have been eliminated, and the relaxation process appears now as an initial value problem. Eqs. (3.13) and (3.14) are, of course, the generalization of (2.53a) and (2.54). Indeed, this present section has just rewritten equations from sections 2.5 and 2.6 as matrix equations. Life is that simple. Sometimes.

We have given these considerations in an operational form which has a clear and simple classical limit. Indeed, since  $\hbar$  occurs explicitly only in the definition (3.4) of the response function, we obtain the corresponding classical expressions by replacing (3.4) by

$$\chi_{ij}''(\vec{k}, \vec{r}, t') = \langle \frac{i}{2} [A_i(\vec{r}, t), A_j(\vec{r}', t')] \rangle_{p. B.} \text{ classically.} \quad (3.15)$$

Otherwise, the whole development above goes through unchanged. The Poisson

bracket appears thus as usual as the classical equivalent of a commutator divided by  $i\hbar$ , in case the observables in question have, themselves, a clear classical meaning (Dirac, 1958). The definition of the Poisson bracket is the standard one. Classically, the dynamical variables  $A_i(\vec{r}, t)$  are functions of the canonical positions  $\vec{r}^{\alpha}$  and momenta  $\vec{p}^{\alpha}$  of all particles, at some common time, say  $t = 0$ . Then

$$[A_i(\vec{r}, t), A_j(\vec{r}', t')]_{P.B.} \equiv \sum_{\alpha} \left( \frac{\partial A_i(\vec{r}, t)}{\partial \vec{r}^{\alpha}} \frac{\partial A_j(\vec{r}', t')}{\partial \vec{p}^{\alpha}} - \frac{\partial A_i(\vec{r}, t)}{\partial \vec{p}^{\alpha}} \frac{\partial A_j(\vec{r}', t')}{\partial \vec{r}^{\alpha}} \right), \quad (3.16)$$

where  $A_i(\vec{r}, t) \equiv A_i(\vec{r}, t; \dots, \vec{r}^{\alpha}, \vec{p}^{\alpha}, \dots)$ . To demonstrate these statements, one starts from the Liouville equation

$$\partial_t \rho(t) = [X(t), \rho(t)]_{P.B.} \quad \text{with } \rho(t=-\infty) = \rho^0, \quad (3.17)$$

where classically the density matrix  $\rho(t)$  becomes the N-particle phase space distribution function,  $\rho(t) \equiv \rho(t; \dots, \vec{r}^{\alpha}, \vec{p}^{\alpha}, \dots)$ , in terms of which averages are defined as usual,

$$\langle A(\vec{r}, t) \rangle = \text{Tr}_{cl} \rho(t) A(\vec{r}, t) / \text{Tr}_{cl} \rho(t). \quad (3.18)$$

Here,  $\text{Tr}_{cl}$  is the classical phase space integral. The reader might find it a useful exercise to solve (3.17) to first order in the external fields, and so recover the equations of this section.

### 3.2. Symmetry Properties

The matrix of response functions has a number of symmetry properties which can be directly obtained from its microscopic definition (3.4). The derivation of these properties is quite straightforward, and we leave it as an exercise. The weary will find some help in the paper by Kadanoff and Martin (1963).

#### 3.2.1 General Properties

An equilibrium system is time translation invariant, so that

$$X_{ij}^{\alpha}(\vec{r}, t; \vec{r}', t') = X_{ij}^{\alpha}(\vec{r}, t; \vec{r}', t-t'). \quad (3.19)$$

Therefore, a Fourier transform  $X_{ij}^{\alpha}(\vec{r}, \vec{r}'; \omega)$  with respect to the time difference variable can be defined.

Three additional properties reflect the fact that  $X_{ij}^{\alpha}$  is a commutator of hermitian operators  $A_i(\vec{r}, t)$  which have, by assumption, a definite signature  $\epsilon_i$  under time reversal. They are

$$X_{ij}^{\alpha}(\vec{r}, t; \vec{r}', t') = -X_{ij}^{\alpha}(\vec{r}', t'; \vec{r}, t) \quad (\text{commutator}) \quad (3.20a)$$

$$= -[X_{ij}^{\alpha}(\vec{r}, t; \vec{r}', t')]^* \quad (\text{hermiticity}) \quad (3.20b)$$

$$= -\epsilon_i \epsilon_j X_{ij}^{\alpha}(\vec{r}, -t; \vec{r}', -t') \quad (\text{time reversal}), \quad (3.20c)$$

or for the Fourier transform

$$X_{ij}^{\alpha}(\vec{r}, \vec{r}'; \omega) = -X_{ij}^{\alpha}(\vec{r}', \vec{r}; -\omega) \quad (3.21a)$$

$$= -[X_{ij}^{\alpha}(\vec{r}, \vec{r}'; -\omega)]^* \quad (3.21b)$$

$$= -\epsilon_i \epsilon_j X_{ij}^{\alpha}(\vec{r}, \vec{r}'; -\omega). \quad (3.21c)$$

$\epsilon_i$  is +1 for the mass or energy density, e.g., and -1 for the momentum or spin density. (3.20c) and (3.21c) hold for systems for which both the Hamiltonian and the ensemble are time reversal invariant, the situation most frequently encountered. Of course, if the system is in a magnetic field  $\vec{B}$ , this changes sign under time reversal so that (3.20c), (3.21c) more generally read

$$\chi_{ij}''(\vec{r}, t; \vec{r}', t'; \vec{B}) = -e_i^T e_j^T \chi_{ij}''(\vec{r}, -t; \vec{r}', -t'; -\vec{B}), \quad (3.22a)$$

$$\chi_{ij}''(\vec{r}, t; w; \vec{B}) = -e_i^T e_j^T \chi_{ij}''(\vec{r}, t; -w; -\vec{B}). \quad (3.22b)$$

$\vec{B}$  need not be an external field. In a ferromagnet, it might be the spontaneously produced internal field. Namely, while in a ferromagnet, in the absence of external fields, the Hamiltonian is invariant under time reversal, the state is not. If you turn all spins backwards, the axis of the spontaneous magnetization will flip over.

### 3.2.2 Isotropic Systems

We will be mostly concerned with isotropic systems which are, in addition, invariant under spatial translations, rotations, and reflections (parity).

Then

$$\chi_{ij}''(\vec{r}, t; \vec{r}', t') = \chi_{ij}''(\vec{r}-\vec{r}', t-t') \quad (3.23)$$

$$= e_i^P e_j^P \chi_{ij}''(-\vec{r}, t; -\vec{r}', t') \quad (\text{parity}), \quad (3.24)$$

where  $e_i^P$  is the signature of  $A_i(\vec{r}, t)$  under parity; i.e.,  $e_i^P = 1$  for the mass and energy density, spin etc., and  $e_i^P = -1$  for the momentum density. Corresponding relations hold for the Fourier transforms,  $\chi_{ij}''(\vec{k}, w)$ .

It is useful to separate the various symmetry properties into their effects on  $\vec{k}, w$ , and the variable indices  $i, j$ . We get

$$\begin{aligned} \chi_{ij}''(\vec{k}, w) &= e_i^T e_j^T e_i^P e_j^P [\chi_{ij}''(\vec{k}, w)]^* = e_i^T e_j^T e_i^P e_j^P \chi_{ij}''(\vec{k}, w) \\ &= -e_i^T e_j^T \chi_{ij}''(\vec{k}, -w) = e_i^P e_j^P \chi_{ij}''(-\vec{k}, w). \end{aligned} \quad (3.25)$$

Consequently,  $\chi_{ij}''(\vec{k}, w)$  is either real and symmetric in  $i \leftrightarrow j$ , or imaginary and

antisymmetric. Usually the former; one of the few correlation functions  $\chi''(\vec{k}, w)$  of some practical use which is imaginary is that which links the momentum density  $\vec{g}$  with the spin density  $\vec{S}$ .

We have not yet used rotational invariance. In this case, little is to be gained from general formulae. Yet, the matter is simple enough. For example, the density-density correlation function  $\chi_{nn}''(\vec{k}, w)$  in a liquid must be a scalar. But there is only one scalar that one can form from  $\vec{k}$ :  $k^2$ . Thus,  $\chi_{nn}''(\vec{k}, w)$  must be a function of  $k = |\vec{k}|$  only. Or consider the momentum density correlation function

$$\chi_{g_i g_j}''(\vec{k}, w). \quad \text{It must be a tensor. Now from } \vec{k}, \text{ one can form three tensors: } \delta_{ij}, k_i k_j, \text{ and } \epsilon_{ijk} k_k \text{ where } \delta_{ij} \text{ is the Kronecker symbol, and } \epsilon_{ijk} \text{ the Levi-Civita symbol. Thus}$$

$$\chi_{g_i g_j}''(\vec{k}, w) = \delta_{ij} A(k, w) + k_i k_j B(k, w) + \epsilon_{ijk} k_k C(k, w), \quad (3.26)$$

where the three functions  $A, B$ , and  $C$  depend only on  $k = |\vec{k}|$ . Actually  $C(k, w) = 0$  since  $\chi_{g_i g_j}''$  is even under parity. So this is how symmetry is used.

### 3.2.3. Crystals

An ideal crystal is, of course, not invariant under arbitrary translations and rotations but only under those which bring every lattice point into an equivalent position within the lattice. This means, in particular, that (3.23) is no longer true. A Fourier transform must now contain two wavevectors of which one is discrete, reflecting the periodicity of the lattice. The matter is essentially trivial.

One normally gets by with

$$\chi_{ij}''(\vec{k}, w) = V^{-1} \int d\vec{r} \int d\vec{r}' e^{-i\vec{k}(\vec{r}-\vec{r}')} \chi_{ij}''(\vec{r}, \vec{r}'; w), \quad (3.27)$$

if one uses experimental probes whose wavelength  $2\pi/k$  is much larger than the lattice constant.

3.3 Positivity of  $w X_{ij}^w(x)$  and Dissipation

In section 2.8, we proved an important positivity property, namely that  $w X^w(k_w)$  is non-negative, in a fashion that easily applies to multivariate functions. The general statement is that, for any stable system,  $w X_{ij}^w(r, r'; w)$  is positive (semi-) definite if considered as a supermatrix with indices  $i, r$  and  $j, r'$ . Or in translationally invariant systems,

$$\sum_{i,j} \alpha_i^* w X_{ij}^w(k_w) \alpha_j \geq 0 \quad \text{for all } \vec{k} \text{ and } w, \tag{3.28}$$

for arbitrary  $\alpha_i$ . Our previous proof was statistical, involving the fluctuation-dissipation theorem which continues to hold true here. It is very instructive, however, to consider the matter by an alternative, dynamical route which is taken from Kadanoff and Martin (1963), and inquires into the dynamical significance of (3.28). We consider the total energy,  $W(t) = \text{tr } \rho(t) \mathcal{K}(t)$ , and its rate of change

$$\begin{aligned} \frac{dW}{dt} &= \text{tr } \rho(t) \frac{\partial \mathcal{K}(t)}{\partial t} = -\sum_i \int d\vec{r} [\text{tr } \rho(t) A_i(\vec{r}, t)] \frac{\partial}{\partial t} \theta_{\alpha_i}^{\text{ext}}(\vec{r}, t) \\ &= -\sum_i \int d\vec{r} \langle [A_i(\vec{r}, t)]_{\text{eq}} \rangle + \theta \langle A_i(\vec{r}, t) \rangle \frac{\partial}{\partial t} \theta_{\alpha_i}^{\text{ext}}(\vec{r}, t) \end{aligned} \tag{3.29}$$

Only the external change,  $\sim \partial_t \theta_{\alpha_i}^{\text{ext}}(t)$ , contributes. The internal change,  $\sim \text{tr } \rho(t) \mathcal{K}(t) = (i\hbar)^{-1} \text{tr } [\rho(t), \mathcal{K}(t)] \mathcal{K}(t)$ , vanishes. The equilibrium term in (3.29) does not contribute, on the average. The total work done on the system must be positive, and it is given by

$$\Delta W = \int_{-T}^T dt \frac{dW}{dt} = \sum_i \int_{-T}^T dt \int d\vec{r} \theta_{\alpha_i}^{\text{ext}}(\vec{r}, t) \frac{\partial}{\partial t} \theta \langle A_i(\vec{r}, t) \rangle, \tag{3.30}$$

where  $T$  is so large that the external fields vanish before  $-T$  and after  $T$ . Using the

3.3 Positivity of  $w X_{ij}^w(w)$  and Dissipation

Wiener-Kinchin theorem (which is simply the statement that  $\int_{-T}^T dt A^*(t)B(t) = \int_{-2T}^{2T} A^*(x)B(x)$ ) and the general result (3.7), we obtain, to order  $(\delta\alpha)^2$ ,

$$\Delta W = \int_{-2T}^{2T} \frac{rdk}{2\pi} \frac{rdk'}{3} (-i) \sum_{i,j} \delta\alpha_i^*(k^*) w X_{ij}^w(k, j) \delta\alpha_j(k^*), \tag{3.31}$$

where  $X_{ij}^w(k, j)$  is as given in (3.7a). The fields  $\delta\alpha_i(\vec{r}, t)$  are real so that  $\delta\alpha_i^*(k, j) = \delta\alpha_i(-k, -j)$ . Hence the principal value part of  $w X_{ij}^w(k, j)$ , eq. (3.7a) which is odd under  $\vec{k}, j \rightarrow -\vec{k}, -j$ , does not contribute to (3.31). We therefore obtain

$$\Delta W = \int_{-2T}^{2T} \frac{rdk}{2\pi} \frac{rdk'}{3} \sum_{i,j} \delta\alpha_i^*(k^*) w X_{ij}^w(k, j) \delta\alpha_j(k^*) \geq 0, \tag{3.32}$$

which must be positive in a dissipative system. Since the external fields can be arbitrarily chosen, we obtain eq. (3.28).

Of course, our conclusion holds only in a stable system. In network theory, one would say it holds in a "passive network". A laser is not dissipative after being pumped, and (3.28) will fail at the lasing frequency. However, the equation (3.28) will certainly be true for any system which is in thermal equilibrium. Undercooled liquids? Yes, for those it holds, too. (3.28) indicates stability with respect to infinitesimal disturbances. In this sense, an undercooled liquid is quite stable (metastable). You have to shake it, softly but with some determination, to make it crystallize.

3.4 Sum Rules

Exactly as in section 2.9, one obtains from (3.4)

$$\begin{aligned} \int_{\frac{dw}{2\pi}} w X_{ij}^w(r, r'; w) &= \langle \frac{1}{\hbar} [ \partial_t^0 A_i(\vec{r}, t), A_j(\vec{r}', t) ] \rangle \\ &= \langle \frac{1}{\hbar} [ [A_i(\vec{r}, t), H], \dots, H, A_j(\vec{r}', t) ] \rangle. \end{aligned} \tag{3.33}$$



These expressions, which can be exactly evaluated in some cases, furnish coefficients for a large  $z$  expansion of the response functions  $X_{ij}(iz)$ . Their practical importance is in their use for interpolation schemes as discussed in sections 2.10, 11, since the sum rules represent essentially the only results of numerical use which can be rigorously obtained from first principles. The most important sum rule, similar to eq. (2.78), is the  $f$ -sum rule for the particle density correlation function,

$$\int \frac{d\omega}{\pi} \omega X_{nn}''(\vec{r}, \vec{r}'; \omega) = \frac{1}{m} (\vec{\nabla} \cdot \vec{\nabla}') \langle n(\vec{r}) \rangle \delta(\vec{r} - \vec{r}') \quad (3.34a)$$

or

$$\int \frac{d\omega}{\pi} \omega X_{nn}''(\vec{k}, \omega) = \frac{n}{m} k^2, \quad (3.34b)$$

for a translationally invariant system. Its proof is obvious from the analogous proof of eq. (2.78).

### 3.5 The Fluctuation-Dissipation Theorem

Here again, we have done all the work in section 2.7. If we define fluctuation functions in thermal equilibrium by

$$S_{ij}(\vec{r}, \vec{r}'; \omega) = \int_{-\infty}^{\infty} dt (t-t') e^{i\omega(t-t')} \langle \langle A_i(\vec{r}, t) - \langle A_i(\vec{r}, t) \rangle \rangle \langle A_j(\vec{r}', t') - \langle A_j(\vec{r}', t') \rangle \rangle \rangle, \quad (3.35)$$

we obtain from eq. (2.67b)

$$X_{ij}''(\vec{r}, \vec{r}'; \omega) = (2\hbar)^{-1} (1 - e^{-\hbar\omega\beta}) S_{ij}(\vec{r}, \vec{r}'; \omega), \quad (3.36a)$$

or

$$X_{ij}''(\vec{k}, \omega) = (2\hbar)^{-1} (1 - e^{-\hbar\omega\beta}) S_{ij}(\vec{k}, \omega), \quad (3.36b)$$

### 3.5 The Fluctuation-Dissipation Theorem

in a translationally invariant system. Another useful function is the symmetrized fluctuation function

$$\varpi_{ij}(\vec{r}, \vec{r}'; t-t') = \langle \frac{1}{2} \{ A_i(\vec{r}, t), A_j(\vec{r}') \} \rangle - \langle A_i(\vec{r}, t) \rangle \langle A_j(\vec{r}', t') \rangle, \quad (3.37)$$

whose Fourier transform  $\varpi_{ij}(\omega)$  is given by

$$\varpi_{ij}(\vec{r}, \vec{r}'; \omega) = \hbar \coth(\hbar\omega\beta/2) X_{ij}''(\vec{r}, \vec{r}'; \omega), \quad (3.38)$$

and so its symmetry properties can be inferred from those of  $X_{ij}''(\omega)$ .

Classically, the functions  $S$  and  $\varpi$  are identical, and the fluctuation-dissipation theorem becomes

$$X_{ij}''(\vec{r}, \vec{r}'; \omega) = (\beta/2) \varpi_{ij}(\vec{r}, \vec{r}'; \omega) \quad \text{classically} \quad (3.39a)$$

or

$$X_{ij}''(\vec{r}, \vec{r}'; t-t') = (\beta/2) i \partial_t S_{ij}(\vec{r}, \vec{r}'; t-t'). \quad (3.39b)$$

It is a useful exercise to derive eqs. (3.39) classically, without taking the detour via quantum mechanics. For some help, see Martin (1968).

The name of the celebrated theorem is now clear. It relates, for any system in thermal equilibrium, two physically distinct quantities of fundamental experimental significance: the spontaneous fluctuations on the one hand which arise, even in the absence of external forces, from the thermal motion of the constituent particles. Described by  $S$ , these fluctuations give rise to the scattering of neutrons or light. And the dissipative behavior of many-body systems, on the other hand, describing the fact that all or part of the work done by external stirring forces is irreversibly disseminated into the infinitely many degrees of freedom of thermal systems. This characteristic property is described by  $X''$  as we saw in the last section. The former property is an essentially statistical one (albeit ultimately of mechanical origin), the latter property is an essentially mechanical

one (albeit not without statistical implications).

Our proof has been based, specifically, on the canonical ensemble  $\sim e^{-\beta H}$ ; it goes through unchanged in the grand canonical ensemble  $\sim e^{-\beta(H-\mu N)}$  as well.

In fact, as our discussion of neutron scattering after (2.63) indicates, the theorem is more generally valid. Its fundamental connection with detailed balancing can be exploited in a dynamical proof. Indeed, in a sense the theorem can be used to introduce temperature into a correlation function description. This is its fundamental significance, most clearly recognized in the Green's function techniques developed by Martin and Schwinger (1959) and others. See also Kadanoff and Baym (1962).

This remark is of practical import for systems such as ferromagnets or superfluids in which there is spontaneous order present. If such systems are described by the canonical or grand canonical ensemble, the fluctuation-dissipation theorem fails for certain variables. What has to be done, then, is to restrict the ensemble (by specifying order parameters) in such a fashion that the theorem is reinstated again. We shall discuss examples of this procedure.

We end this section with another but related remark. There are two features which enter any theory of many-particle systems: one which is mechanical, summarized in the Schrödinger equation or Newton's equations of motion, and one which is statistical, summarized in the averaging recipe over a properly chosen ensemble. The former is straightforward in principle though formidable in practice, the latter is much more subtle. These two aspects can, of course, never be completely disentangled.

However, as we have pointed out above, the response function  $X''(\vec{r}, \vec{r}'; t)$  is largely a mechanical quantity. This is indicated by our derivation of linear response which is characterized by  $X''$ , a purely mechanical derivation which makes but implicit reference to statistical questions. It is very clearly indicated by the

### 3.5 The Fluctuation-Dissipation Theorem

$f$ -sum rule (2.78) which holds in any stationary ensemble, expression nothing but the conservation law (2.3) and the commutator (2.77). The fluctuation functions  $S(\vec{r}, \vec{r}'; t)$  or  $\omega(\vec{r}, \vec{r}'; t)$  are much more statistical. Even in their definitions, eqs. (3.37) or (3.37), we had to subtract constant terms to avoid contributions  $\sim \delta(u)$  in their spectrum, and we had to argue that because of the presumed statistical independence of  $A(\vec{r}, t)$  from  $A(\vec{r}', t')$  for large  $|\vec{r}-\vec{r}'|$ , these terms were given by  $\langle \Delta \rangle^2$ . This assumption is one of ergodicity or more precisely, "mixing" which implies ergodicity (Lebowitz 1972), and it is a subtle affair. It is best, therefore, to be theoretical considerations upon the more mechanical and straightforward response functions  $X''(\vec{r}, \vec{r}'; t)$ , inferring fluctuation properties later from the Nyquist theorem.

The response functions  $X''$  have an additional property which is very welcome in systems with long-ranged order (superfluids etc.). We will always be interested in local observables  $A(\vec{r})$ , i.e., variables which depend only on properties (position, momentum, spin) of particles in a small neighborhood of  $\vec{r}$ . Even for quantum systems in which particles are indistinguishable, this is a valid concept:  $A(\vec{r})$  depends only on creation and annihilation fields  $\psi^+(\vec{r}, t)$ ,  $\psi(\vec{r}, t)$   $|\vec{r}-\vec{r}'|$  small, say of the order of the force range. This means that the commutator  $[A_1(\vec{r}), A_2(\vec{r}')] ]$ , vanish if  $\vec{r}'$  is far from  $\vec{r}$ , and therefore the functions  $X''_{ij}(\vec{r}, \vec{r}'; t=0)$  and their time derivatives at  $t=0$ , or else the sum rules

$$\int_{\frac{d\omega}{2\pi}} \omega^n X''_{ij}(\vec{r}, \vec{r}'; \omega), \quad n \geq 0, \quad (3.40)$$

fall off very rapidly as  $|\vec{r}-\vec{r}'| \rightarrow \infty$ . They are of short range. One might argue quantum-mechanically, that the commutator function  $X''_{ij}(\vec{r}, \vec{r}'; t)$  ought to vanish if  $\vec{r}'$  is far from  $\vec{r}$  since then, measurements of  $A_1(\vec{r}, t)$  and  $A_2(\vec{r}', t')$  do not interfere. This is not always true of the statistical functions, e.g.,

$$S_{ij}(\vec{r}, \vec{r}'; t=0) = \int_{\frac{d\omega}{2\pi}} S_{ij}(\vec{r}, \vec{r}'; \omega). \quad (3.41)$$

It is a fundamental property of ordered systems that certain functions of this type fall off very slowly as  $|\vec{r}-\vec{r}'| \rightarrow \infty$ , as  $|\vec{r}-\vec{r}'|^{-3}$  (vide, the momentum density correlation function in superfluids, chapter 10) or even as  $|\vec{r}-\vec{r}'|^{-1}$  (vide, the transverse spin correlation function in ferromagnets, chapter 7). This appearance of long-ranged order can, of course, not be avoided, it is real and of great experimental significance. However, the static correlation function  $S(\vec{r}, \vec{r}', t=0)$  is essentially a time integral over the function  $X''(\vec{r}, \vec{r}', t)$ , as seen from the formal expression (2.67a) or more clearly the classical equation (3.39b). In a formulation based on  $X''$ , the long-ranged nature of correlations appears therefore, properly, as a cumulative effect.

It is helpful in this respect to introduce yet another correlation function  $C(t)$  defined so that (3.39b) is true quantum-mechanically, i. e., so that

$$i\partial_t C_{ij}(\vec{r}, \vec{r}', t) = (2/\beta) X''_{ij}(\vec{r}, \vec{r}', t). \quad (3.42)$$

This is the Kubo function (Kubo 1959), and it can be written in the form

$$C_{ij}(\vec{r}, \vec{r}', t) = \beta^{-1} \int_0^\beta d\beta' \langle [A_i(\vec{r}, t) A_j(\vec{r}', t' + i\beta')] \rangle - \langle A_i \rangle \langle A_j \rangle, \quad (3.43)$$

as one shows easily from the fluctuation-dissipation theorem. We have already encountered its Laplace transform

$$C_{ij}(\vec{r}, \vec{r}', z) = \int_0^\infty dt e^{izt} C_{ij}(\vec{r}, \vec{r}', t) \quad (\text{for } \text{Im}z > 0) \quad (3.44a)$$

$$= \beta^{-1} \int \frac{d\omega}{\pi i} \frac{X''_{ij}(\vec{r}, \vec{r}', \omega)}{\omega(\omega-z)} \quad (\text{for } \text{Im}z \neq 0) \quad (3.44b)$$

$$= (1/i2\beta) [X_{ij}(\vec{r}, \vec{r}', z) - X_{ij}(\vec{r}, \vec{r}', i0)], \quad (3.44c)$$

which describes relaxation in the most direct fashion.

With the last few remarks, we are a few steps ahead of the development since the system treated in the next chapter, the normal fluid, does not exhibit any long-ranged order. Who, though, would not like a little advance notice of future complications?

In analogy to magnetic neutron scattering as discussed before, the scattered intensity is given by

$$I_{\text{scatt.}} \left( \begin{matrix} \vec{k}_i \rightarrow \vec{k}_i - \vec{k} \\ \omega_i \rightarrow \omega_i - \omega \end{matrix} \right) = [\text{factors times}] S_{nn}(\vec{k}, \omega) \quad (4.1)$$

as shown in the Appendix. The bracket contains kinematical factors which are important for our purpose.

Light scattering experiments have been performed on many liquids and gases (see, for example, the recent book by Berne and Pecora 1973), and at frequencies the spectrum found looks as shown in fig. 4.2.

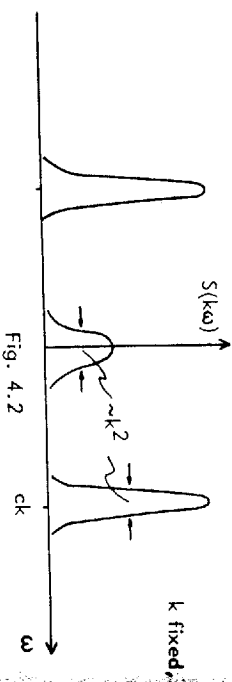


Fig. 4.2

There are three Lorentzian peaks, the central "Rayleigh peak" (caused by sound diffusion) and two symmetrically displaced "Brillouin peaks" (caused by sound waves). Much of the effort in this chapter will go into deriving this spectrum.

Since the wavelength of light is so long compared to interatomic distances in a liquid, we expect that a continuum theory will be sufficient to explain this spectrum. Indeed, we will derive it in all detail from the phenomenological, linearized Navier-Stokes equations of fluid dynamics, obtained, in chapter 2, a simple Lorentzian spectrum for magnetization fluctuations from the spin diffusion equation (2.7). (In fact, as will be more apparent in presentation, which follows the paper by Kadomoff and Martin 1963, is tanta

THE NORMAL FLUID

CHAPTER 4

In this chapter we will use the methods developed above, to analyze fluctuations in a normal (isotropic, not superfluid) liquid or gas. Of interest are fluctuations of several physical quantities: the particle number, momentum, energy and entropy densities, and a few others. The most important of these are density fluctuations whose spectral function is given by

$$S_{nn}(\vec{k}, \omega) = \int_{-\infty}^{\infty} dt \int d\vec{r} e^{i(\vec{k}\cdot\vec{r} - \omega t - i\epsilon t)} \langle n(\vec{r}, t) n(\vec{0}, 0) \rangle, \quad (4.1)$$

where  $n(\vec{r}, t)$  is the particle density operator,  $n = \langle n(\vec{r}, t) \rangle_{\text{eq}}$ , the equilibrium value of the density.

$S_{nn}(\vec{k}, \omega)$  is called the dynamical structure factor, and it is one of the most important quantities in the theory of many-particle systems. It is the density fluctuation spectrum that is measured in inelastic light, X-ray, and neutron scattering experiments, to name only a few applications. In a typical light scattering experiment, for example, one sends a laser beam of frequency  $\omega_i$  and wave vector  $\vec{k}_i$  into a liquid cell. One then looks for scattered light with frequency  $\omega_f = \omega_i - \omega$  and wave vector  $\vec{k}_f = \vec{k}_i - \vec{k}$ , see fig. 4.1.

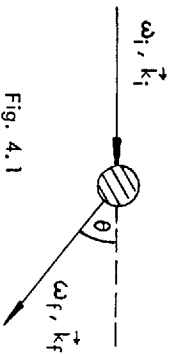


Fig. 4.1

$$\begin{aligned} \omega_f &= \omega_i - \omega \\ \vec{k}_f &= \vec{k}_i - \vec{k} \\ |k| &= 2|k_i| \sin(\theta/2) \end{aligned} \quad (4.2)$$

a derivation of the equations of hydrodynamics, a fact which does not seem to be generally appreciated.)

Fig. 4.2 contains an experimental clue that shows that a hydrodynamic theory should be sufficient: the widths of the three peaks are measured to be proportional to  $k^2$ ; they become extremely narrow in forward scattering as  $k \rightarrow 0$ . Consequently, each of the peaks must reflect a collective process whose lifetime  $\tau(k) \sim k^{-2}$  becomes infinite as  $k \rightarrow 0$ : the trademark of a hydrodynamic process.

Now we saw in section 2.1 that there is a hydrodynamic process associated with each conserved local variable. And so we begin with the five continuity equations for the particle density  $n(\vec{r}, t)$ , the momentum density  $\vec{g}(\vec{r}, t)$ , and the energy density  $e(\vec{r}, t)$ :

$$\partial_t n(\vec{r}, t) + \nabla \cdot \vec{g}(\vec{r}, t)/m = 0 \quad \text{number conservation,} \quad (4.4a)$$

$$\partial_t \vec{g}_i(\vec{r}, t) + \nabla_j \tau_{ij}(\vec{r}, t) = 0 \quad \text{momentum conservation,} \quad (4.4b)$$

$$\partial_t e(\vec{r}, t) + \nabla \cdot \vec{j}^e(\vec{r}, t) = 0 \quad \text{energy conservation.} \quad (4.4c)$$

Here,  $\vec{j}^e$  is the microscopic energy current density (operator), and the microscopic stress tensor  $\tau_{ij}$  functions as the current for the momentum.

For definiteness, let us write down microscopic expressions for these quantities even though we will make little explicit use of them. We take the case of a "simple" liquid, i. e., an assembly of identical point particles of mass  $m$  which interact through a central pair potential  $v(r) = v(|\vec{r}|)$  which is of short range.

For the noble gases like argon, this is adequate. The Hamiltonian is then

$$H = \sum_{\alpha} \frac{p_{\alpha}^2}{2m} + \frac{1}{2} \sum_{\alpha, \beta} v(|\vec{r}_{\alpha} - \vec{r}_{\beta}|). \quad (4.5)$$

And the microscopic expressions for a classical system (quantum-mechanically,

they simply have to be symmetrized in  $\vec{r}^{\alpha}$  and  $\vec{p}^{\alpha}$ , as in (2.4)) are the following:

$$n(\vec{r}, t) = \sum_{\alpha} \delta(\vec{r} - \vec{r}^{\alpha}), \quad (4.6)$$

$$\vec{g}_i(\vec{r}, t) = \sum_{\alpha} p_i^{\alpha} \delta(\vec{r} - \vec{r}^{\alpha}),$$

$$e(\vec{r}, t) = \sum_{\alpha} \left[ \frac{p_{\alpha}^2}{2m} + \frac{1}{2} \sum_{\beta \neq \alpha} v(r^{\alpha\beta}) \right] \delta(\vec{r} - \vec{r}^{\alpha}),$$

$$\tau_{ij}(\vec{r}, t) = \sum_{\alpha} \left[ \frac{p_i^{\alpha} p_j^{\alpha}}{m} \delta(\vec{r} - \vec{r}^{\alpha}) - \frac{1}{2} \sum_{\alpha \neq \beta} r_i^{\alpha\beta} v_i(r^{\alpha\beta}) \int_0^1 d\lambda \delta\left(\vec{r} - \frac{\vec{r}^{\alpha} + \vec{r}^{\beta}}{2} - \frac{\lambda}{2} \vec{r}^{\alpha\beta}\right), \right.$$

$$\left. - \sum_{\alpha \neq \beta} \frac{1}{4m} \frac{p_i^{\alpha\beta} v_i(r^{\alpha\beta}) (p_i^{\alpha} + p_i^{\beta})}{r_i^{\alpha\beta}} \int_0^1 d\lambda \delta\left(\vec{r} - \frac{\vec{r}^{\alpha} + \vec{r}^{\beta}}{2} - \frac{\lambda}{2} \vec{r}^{\alpha\beta}\right), \right]$$

where  $\vec{r}^{\alpha\beta} = \vec{r}^{\alpha} - \vec{r}^{\beta}$  and  $v_i(r) = \nabla_i v(r)$ , and where the positions  $\vec{r}^{\alpha}$  and momenta  $\vec{p}^{\alpha}$  of all particles are to be taken at time  $t$ . For clarity, all vector arrows have been omitted. Similar if a little more complicated expressions can be written down for a molecular liquid. In fact, all the hydrodynamic results obtained in this chapter are rigorously valid for isotropic molecular liquids, too.

The method used in this chapter is the one presented in chapter 2. A different approach which we will develop in later chapters, is applied to superfluids in chapter 10 and can easily be used for the description of normal fluids as well.

#### 4.1 The Equations of Fluid Dynamics

The continuity equations are microscopically rigorous but they do not yet make a complete theory. As in the spin diffusion case, they have to be supplemented by macroscopic constitutive relations. In order to have all the equations together which constitute the linearized hydrodynamic theory, we

shall write them all down first, and then explain.

Conservation Laws:

$$\partial_t n(\vec{r}, t) + \vec{\nabla} \cdot \vec{g}(\vec{r}, t)/m = 0, \tag{4.7a}$$

$$\partial_t g_i(\vec{r}, t) + \nabla_j \tau_{ij}(\vec{r}, t) = 0, \tag{4.7b}$$

$$\partial_t \epsilon(\vec{r}, t) + \vec{\nabla} \cdot \vec{e}(\vec{r}, t) = 0. \tag{4.7c}$$

Constitutive Relations:

$$\langle \vec{g}(\vec{r}, t) \rangle = mn \vec{v}(\vec{r}, t), \tag{4.8a}$$

$$\langle \tau_{ij}(\vec{r}, t) \rangle = p(\vec{r}, t) \delta_{ij} - n \left[ \nabla_j v_i(\vec{r}, t) + \nabla_i v_j(\vec{r}, t) - \frac{2}{3} \nabla \cdot \vec{v}(\vec{r}, t) \delta_{ij} \right] \tag{4.8b}$$

$$- \zeta \nabla \cdot \vec{v}(\vec{r}, t) \delta_{ij},$$

$$\langle \vec{e}(\vec{r}, t) \rangle = (\epsilon + p) \vec{v}(\vec{r}, t) - \kappa \vec{\nabla} T(\vec{r}, t). \tag{4.8c}$$

Thermodynamic Relations:

$$\vec{\nabla} p(\vec{r}, t) = \left( \frac{\partial p}{\partial n} \right)_\epsilon \vec{\nabla} \langle n(\vec{r}, t) \rangle + \left( \frac{\partial p}{\partial \epsilon} \right)_n \vec{\nabla} \langle \epsilon(\vec{r}, t) \rangle, \tag{4.9a}$$

$$\vec{\nabla} T(\vec{r}, t) = \left( \frac{\partial T}{\partial n} \right)_\epsilon \vec{\nabla} \langle n(\vec{r}, t) \rangle + \left( \frac{\partial T}{\partial \epsilon} \right)_n \vec{\nabla} \langle \epsilon(\vec{r}, t) \rangle. \tag{4.9b}$$

Here  $n, \epsilon, p$  are the equilibrium values of density, energy density, and pressure, e.g.,  $n = \langle n(\vec{r}, t) \rangle$ .  $p(\vec{r}, t)$ ,  $T(\vec{r}, t)$ , and  $\vec{v}(\vec{r}, t)$  are the local values of pressure, temperature, and (average) velocity, in the non-equilibrium flow state. The coefficients in (4.9) are normal thermodynamic derivatives. And the three transport coefficients in (4.8) are called shear viscosity ( $\eta$ ), bulk viscosity ( $\zeta$ ), and heat conductivity ( $\kappa$ ).

These are the Navier-Stokes equations of fluid dynamics. (See, for example, Landau and Lifshitz 1959.) They are linear because we have made them

#### 4.1 The Equations of Fluid Dynamics

that way; more generally, there are terms  $\sim v_j v_i$  in  $\langle \tau_{ij} \rangle$ , for example. However,  $\chi''$  gives the linear response, and so to obtain  $\chi''$  the linearized phenomenological theory is sufficient. Note that the system of equations is now closed. Inserting eqs. (4.8, 9) into (4.7) one obtains 5 coupled equations for the five densities  $\langle n \rangle, \langle g \rangle, \langle \epsilon \rangle$ . These equations involve, of course, a number of coefficients which remain undetermined, namely thermodynamic derivatives and transport coefficients; the parameters of the hydrodynamic theory, just as the spin diffusion coefficient was in chapter 2.

And now to the explanation. Hydrodynamics is valid when, after a brief initial period of rapid and complicated motion, the system has reached local equilibrium, a state in which, for example, the pressure at  $\vec{r}, t$  is at equilibrium with the local values of density and energy density. This state of affairs,  $p_{\text{eq}}(\vec{r}, t) = p_{\text{eq}}(n(\vec{r}, t), \epsilon(\vec{r}, t))$ , is expressed in eqs. (4.9).

The non-derivative, reactive terms in (4.8) are of the same nature, and can be inferred from a Galilei transformation. Generally, the relations between quantities in a stationary medium versus one that moves with constant velocity are given by

$$\vec{g}(\vec{r}, t) = g(\vec{r}-\vec{v}t, t) + \vec{v} m n(\vec{r}-\vec{v}t, t), \tag{4.10a}$$

$$\tau_{ij}(\vec{r}, t) = \tau_{ij}(\vec{r}-\vec{v}t, t) + v_j g_i(\vec{r}-\vec{v}t, t) + v_i v_j m n(\vec{r}-\vec{v}t, t), \tag{4.10b}$$

$$\vec{e}(\vec{r}, t) = \vec{e}(\vec{r}-\vec{v}t, t) + \vec{v} \cdot \left( \tau_{ij}(\vec{r}-\vec{v}t, t) + \epsilon(\vec{r}-\vec{v}t, t) \delta_{ij} \right) + \frac{1}{2} v^2 (g_i^2 + v_i^2 m^2 n^2)(\vec{r}-\vec{v}t, t). \tag{4.10c}$$

As can be easily verified from eqs. (4.6). All quantities with superscript 0 refer to the system at rest, and their arguments are  $(\vec{r}-\vec{v}t, t)$ . But in a normal fluid at rest  $\vec{g} = \vec{v} \delta_{ij} = 0$ , and  $\tau_{ij} = p \delta_{ij}$ . In a system which moves with the local velocity  $\vec{v}(\vec{r}, t)$ , and omitting terms of order  $v^2$ , we obtain the reactive terms of (4.8).

The dissipative terms in (4.8) account for the fact that, for example, a temperature gradient  $\vec{\nabla}T(\vec{r}, t)$  will produce an energy current even if the average velocity is zero. Similarly, the two terms in (4.8b) which are the only ones compatible with isotropic symmetry, account for frictional stresses due to velocity gradients  $\nabla_{ij} v_i$ . A term  $\delta_{ij}^e \sim \lambda(\nabla \times v)_j$  would be possible by rotational symmetry, but is ruled out by parity.

Eqs. (4.8) are thus the result of an expansion of the current densities to first order in gradients of the local conjugate forces  $\vec{v}(\vec{r}, t)$ ,  $T(\vec{r}, t)$ , and  $p(\vec{r}, t)$ . If so, we have to justify the absence of dissipative currents driven by a pressure

gradient. Why are there, more generally, no terms of the form

$$\vec{g}_{ij} = -\lambda \frac{\vec{\nabla} p}{n} - \lambda_{ij} \frac{\vec{\nabla} T}{T}, \quad (4.11a)$$

$$\delta[\vec{r}_i^e - \frac{e+n}{m} \vec{g}_j] = -\lambda_{ij} \frac{\vec{\nabla} p}{n}, \quad (4.11b)$$

which would be allowed by symmetry? The answer is that these terms would violate momentum conservation. To demonstrate this fact is a good but not trivial exercise; note the Onsager relation  $\lambda_{ij} = \lambda_{ji}$ , to be proved below. Actually, this question is much more easily answered in terms of correlation functions, and we will therefore keep it in store until section 4.6. (The argument given by Landau-Lifshitz, 1959, p. 187, is not correct on this point. It is true that  $\lambda_{ij} \cdot \kappa T - \lambda_{ji}^2 \geq 0$  so that if  $\lambda_{ij}$  vanishes,  $\lambda_{ji}$  must vanish, too. But  $\lambda_{ij} = 0$  can only be inferred from the fact that the flux of the particle density, i.e., the momentum current, is itself conserved.)

#### 4.2 Solution of the Hydrodynamic Equations

The Navier-Stokes equations present, in general, a problem of considerable complexity (see e.g., Chandrasekhar 1961). In (4.7-9), we have already simplified this problem enormously by omitting non-linear terms. We shall furthermore eliminate boundary conditions by considering a simply connected medium of infinite extent. In terms of spatial Fourier transforms, we are then faced with a simple initial value problem.

##### 4.2.1. Transverse Fluctuations

Inserting (4.8b) into (4.7b), one obtains

$$\partial_t \langle \vec{g}_t(\vec{r}, t) \rangle + \vec{\nabla} p(\vec{r}, t) - \frac{(\zeta + \eta/3)}{m} \vec{\nabla} (\vec{\nabla} \cdot \langle \vec{g}_t(\vec{r}, t) \rangle) - \frac{\eta}{m} \nabla^2 \langle \vec{g}_t(\vec{r}, t) \rangle = 0. \quad (4.12)$$

This equation separates into a longitudinal and a transverse part. The momentum density  $\vec{g}_t$ , like any vector, can be split up in the form

$$\vec{g}_t(\vec{r}, t) = \vec{g}_L(\vec{r}, t) + \vec{g}_T(\vec{r}, t), \quad (4.13)$$

where

$$\vec{\nabla} \times \vec{g}_L = 0 \quad \text{and} \quad \vec{\nabla} \cdot \vec{g}_T = 0. \quad (4.13a)$$

For the transverse component, we then obtain

$$(\partial_t - \frac{\eta}{m} \nabla^2) \langle \vec{g}_T(\vec{r}, t) \rangle = 0, \quad (4.14)$$

which is our old friend, the diffusion equation. And as we did in section 2.1, we solve by performing the Fourier-Laplace transformation ( $\text{Im}z > 0$ )

$$\langle \vec{g}_T(\vec{k}z) \rangle = \int_0^\infty dt e^{izt} \int d\vec{r} e^{-i\vec{k} \cdot \vec{r}} \langle \vec{g}_T(\vec{r}, t) \rangle. \quad (4.15)$$

The solution of the transverse initial value problem is then

$$\langle \vec{g}_1(\vec{k}, z) \rangle = \frac{1}{z + ik^2 \eta/mn} \langle \vec{g}_1(\vec{k}, t=0) \rangle. \quad (4.16)$$

With the diffusion pole at  $z = -ik^2 \eta/mn$ , in the lower half plane, corresponding to a hydrodynamic lifetime  $\tau(k) = mn/(\eta k^2) \rightarrow \infty$  as  $k \rightarrow 0$ .

#### 4.2.2. Longitudinal Fluctuations

The other equations are only a little more complicated because they

couple the longitudinal variables. By using the constitutive relations (4.8) and the conservation laws (4.7), we find

$$\partial_t \langle n(\vec{r}, t) \rangle + \vec{\nabla} \cdot \langle \vec{g}_2(\vec{r}, t) \rangle / m = 0, \quad (4.17a)$$

$$\partial_t \langle \vec{g}_2(\vec{r}, t) \rangle + \vec{\nabla} p(\vec{r}, t) - (\epsilon + \frac{4}{3} \pi) / (mn) \vec{\nabla} (\vec{\nabla} \cdot \langle \vec{g}_2(\vec{r}, t) \rangle) = 0, \quad (4.17b)$$

$$\partial_t \langle \epsilon(\vec{r}, t) \rangle + (\epsilon + p) \vec{\nabla} \cdot \langle \vec{g}_2(\vec{r}, t) \rangle / (mn) - \kappa \nabla^2 T(\vec{r}, t) = 0. \quad (4.17c)$$

The second equation is really a scalar equation since all of its terms are parallel to  $\vec{\nabla}$ , i.e.,  $\vec{k}$ .

Eqs. (4.17a,c) combine to

$$\partial_t [\langle \epsilon(\vec{r}, t) \rangle - \frac{\epsilon + p}{n} \langle n(\vec{r}, t) \rangle] - \kappa \nabla^2 T(\vec{r}, t) = 0, \quad (4.18)$$

which indicates that it may be convenient to introduce the variable

$$q(\vec{r}, t) \equiv \epsilon(\vec{r}, t) - \frac{\epsilon + p}{n} n(\vec{r}, t) \quad (4.19)$$

in place of the energy density. Its physical significance becomes apparent from the thermodynamic relations (4.9) which, after the usual headache with thermodynamic manipulations, take the form

#### 4.2 Solution of the Hydrodynamic Equations

$$\vec{\nabla} p(\vec{r}, t) = \left( \frac{\partial p}{\partial n} \right)_S \vec{\nabla} \langle n(\vec{r}, t) \rangle + \frac{1}{n} \left( \frac{\partial p}{\partial S} \right)_n \vec{\nabla} \langle q(\vec{r}, t) \rangle, \quad (4.20a)$$

$$\vec{\nabla} T(\vec{r}, t) = \left( \frac{\partial T}{\partial S} \right)_n \vec{\nabla} \langle n(\vec{r}, t) \rangle + \frac{1}{n} \left( \frac{\partial T}{\partial S} \right)_n \vec{\nabla} \langle q(\vec{r}, t) \rangle, \quad (4.20b)$$

where  $S$  is the total entropy. These equations identify  $q(\vec{r}, t)$  as an operator for  $T$  times an entropy density. The corresponding thermodynamic identity is

$$Tn d(S/N) = d\epsilon - \frac{\epsilon + p}{n} dn, \quad (4.21)$$

where  $S/N$  is the entropy per particle.

And now let us, once again, write down the three longitudinal equations (4.17). With (4.19, 20), they become

$$\partial_t \langle n \rangle + \vec{\nabla} \cdot \langle \vec{g}_2 \rangle / m = 0,$$

$$[\partial_t - \frac{4}{3} \pi + \epsilon] / (mn) \langle \vec{g}_2 \rangle + \left( \frac{\partial p}{\partial n} \right)_S \vec{\nabla} \langle n \rangle + \frac{1}{n} \left( \frac{\partial p}{\partial S} \right)_n \vec{\nabla} \langle q \rangle = 0,$$

$$[\partial_t - \kappa \frac{\partial T}{\partial S}] \langle \vec{g}_2 \rangle - \kappa \left( \frac{\partial T}{\partial S} \right)_n \vec{\nabla} \langle n \rangle = 0, \quad (4.22)$$

where we have omitted the arguments  $(\vec{r}, t)$ . These equations are again of the type (2.7) or (4.14), with the minor difference that there are now three of them, compare to simplify their appearance a little, we introduce a few names:

$$D_L = \left( \frac{4}{3} \pi + \epsilon \right) / mn,$$

$$mc_v = \frac{1}{n} \left( \frac{\partial S}{\partial T} \right)_n; \quad mc_p = \frac{1}{n} \left( \frac{\partial S}{\partial T} \right)_p,$$

$$c^2 = \left( \frac{\partial p}{\partial mn} \right)_S = \frac{c_p}{c_v} \left( \frac{\partial p}{\partial mn} \right)_T. \quad (4.23)$$

$D_L$  is called the longitudinal diffusion coefficient.  $mc_v$  and  $mc_p$  are the specific heats per particle, at constant volume and pressure, respectively. And the inv



adiabatic compressibility,  $c^2$ , will be found to be the (square of the) speed of sound.

Again we do a Fourier-Laplace transformation as in (4.15). This brings (4.22) into the matrix form

$$\begin{bmatrix} z & -k/m & 0 \\ -kmc^2 & z + ik^2 D_L & -\frac{V \partial \rho}{T \partial S} \frac{1}{n} k \\ ik^2 \chi \left( \frac{\partial T}{\partial n} \right)_S & 0 & z + ik^2 \frac{\kappa}{mnc_v} \end{bmatrix} \begin{bmatrix} \langle n(\vec{k}z) \rangle \\ \langle q(\vec{k}z) \rangle \\ \langle q(\vec{k}, t=0) \rangle \end{bmatrix} = i \begin{bmatrix} \langle q(\vec{k}, t=0) \rangle \\ \langle q(\vec{k}z) \rangle \\ \langle q(\vec{k}, t=0) \rangle \end{bmatrix} \quad (4.24)$$

For the moment, let us consider this a result, leaving the inversion of the 3 x 3 matrix for homework. However, to get some physics out of what we have, we will inquire into the poles of  $\langle n(\vec{k}z) \rangle$  etc. on the complex z-plane. That means to set the determinant of the matrix in (4.24) equal to zero. For small k, the resulting cubic equation for z is solved with little difficulty, and yields

$$z = \pm ck - \frac{i}{2} k^2 \Gamma \quad (\text{sound poles}), \quad (4.25a)$$

$$z = -ik^2 D_T \quad (\text{heat pole}), \quad (4.25b)$$

up to terms of order  $k^3$ . Here, the heat diffusion constant  $D_T$  is given by

$$D_T = \kappa / mnc_p \quad (4.25c)$$

and the sound attenuation constant  $\Gamma$  by

$$\Gamma = D_L + D_T \left( \frac{c^2}{c_v} - 1 \right) = D_T \left( \frac{c^2}{c_v} - 1 \right) + \left( \frac{4}{3} \eta + \zeta \right) / mn. \quad (4.25d)$$

Note that all three poles lie on the lower half of the complex z-plane which is a

relief for the stability-minded, and that they are all, of course, hydrodynamic:  $\tau(k) \sim k^{-2}$ .

### 4.3 Thermodynamic Sum Rules

We have solved the hydrodynamic initial value problem, obtaining eqs. (4.16) and (4.24) which are of the same form as (3.14), and therefore allow a comparison with the formulation of the same problem in terms of correlation functions. To make that comparison, however, we need the static susceptibilities  $\chi_{ij}(k)$ , at least for small k, which are not determined by the equations of motion. These susceptibilities are instead determined by equilibrium statistical mechanics as we saw already in section 2.4. Before listing them, let us introduce a useful notation. We analyzed the symmetry restrictions on the momentum density correlation function in (3.24). Accordingly, we can separate this function into a longitudinal and a transverse part by

$$\chi_{g_i g_j}''(\vec{k}, \omega) = \frac{k_i k_j}{k^2} \chi_L''(k; \omega) + \left( \delta_{ij} - \frac{k_i k_j}{k^2} \right) \chi_T''(k; \omega). \quad (4.26)$$

This splitting is clearly equivalent to that in eq. (4.13).  $\chi_{L,T}''(k; \omega)$  are real functions of  $k = |\vec{k}|$ , odd in  $\omega$ .

And now the susceptibilities:

$$\lim_{k \rightarrow 0} \chi_{nn}''(k) = \lim_{k \rightarrow 0} \frac{d \chi_{nn}''(k; \omega)}{d \omega} = n \left( \frac{\partial n}{\partial p} \right)_T, \quad (4.27a)$$

$$\lim_{k \rightarrow 0} \chi_{qg}''(k) = \lim_{k \rightarrow 0} \frac{d \chi_{qg}''(k; \omega)}{d \omega} = mnc_p T, \quad (4.27b)$$

$$\lim_{k \rightarrow 0} \chi_{nq}''(k) = \lim_{k \rightarrow 0} \int \frac{d \omega}{\pi} \chi_{nq}''(k; \omega) / \omega = T \left( \frac{\partial n}{\partial T} \right)_p, \quad (4.27c)$$

$$\chi(k) = \int \frac{d^3u}{\pi} \chi''_2(k,u)/u = mn, \quad (4.27d)$$

$$\lim_{k \rightarrow 0} \chi_1(k) = \int \frac{d^3u}{\pi} \chi''_1(k,u)/u = mn, \quad (4.27e)$$

$$\chi_{g_1 n}(k) = \chi_{g_1 q}(k) = 0. \quad (4.27f)$$

The last two equations, (4.27f), are a consequence of time reversal

symmetry. By eq. (3.25),  $\chi''_{g_1 n}(k,u)/u$  and  $\chi''_{g_1 q}(k,u)/u$  are odd functions of  $u$ , and their frequency integral vanishes at all  $k$ .

The three equations, (4.27a-c), follow by an analysis parallel to that given in section 2.4. Considering (4.27a), the fluctuation-dissipation theorem

(3.36) gives

$$\chi_{nn}(k) = \int \frac{d^3u}{2\pi} S_{nn}(k,u) (1 - e^{-t u \beta}) / t u. \quad (4.28)$$

Next, we notice that in the limit as  $k \rightarrow 0$ ,  $S_{nn}(k,u) \sim \delta(u)$  because the total number of particles,  $N = \int d^3r n(r, t)$ , is conserved. Thus we can write

$$\lim_{k \rightarrow 0} \chi_{nn}(k) = \lim_{k \rightarrow 0} \beta \int \frac{d^3u}{2\pi} S_{nn}(k,u) = \lim_{k \rightarrow 0} \beta S_{nn}(k, t=0) \quad (4.29)$$

or

$$\chi_{nn}(k=0) = \beta \langle n(N - \langle N \rangle) \rangle = (\beta/V) \langle (N - \langle N \rangle)^2 \rangle. \quad (4.30)$$

Finally, in a grand canonical ensemble,

$$n = \frac{\langle N \rangle}{V} = \frac{\text{tr } e^{-\beta(H - \mu N)} N / \text{tr } e^{-\beta(H - \mu N)}}{V} \quad (4.31a)$$

and therefore

$$\left( \frac{\partial n}{\partial \mu} \right)_{\beta, V} = (\beta/V) \langle N^2 - \langle N \rangle^2 \rangle = n \left( \frac{\partial n}{\partial \mu} \right)_T. \quad (4.31b)$$

#### 4.3 Thermodynamic Sum Rules

The last equation follows from the thermodynamic identity  $dp = n d\mu + (S/V) dT$  relating the pressure  $p$  to the chemical potential  $\mu$ . This proves (4.27a). The other two thermodynamic sum rules, (4.27b, c), follow similarly but after a bit of thermodynamic manipulation.

We add two remarks. The first which is minor is to point out that formally, whatever  $A$  and  $B$ ,

$$\frac{\partial}{\partial \lambda} \text{tr } e^{-\beta(H - \lambda B)}_{A/\lambda=0} = \text{tr } e^{-\beta H} \int_0^1 dB' e^{\beta' H} B e^{-\beta' H} A, \quad (4.32)$$

from which it follows that, for example,

$$\left( \frac{\partial n}{\partial \mu} \right)_{\beta, V} = \beta C_{nn}(k=0, t=0) = \int \frac{d^3u}{\pi} \chi''_{nn}(k=0, u)/u, \quad (4.33)$$

where  $C_{nn}$  is the Kubo function defined in eq. (3.43). To establish (4.27) therefore, the fluctuation-dissipation theorem is necessary but the conservation laws are not.

The second remark has to do with our choice of ensemble. If we were to interpret (4.30), rashly, in the canonical ensemble which holds the total number of particles fixed, we would find  $\chi_{nn}(k=0) = 0$ . At finite  $k$ , with  $k^{-1}$  small compared to the linear dimensions of the container,  $\chi_{nn}(k)$  describes local fluctuations of the particle density, and is independent of the choice of ensemble (among the proper ensembles: microcanonical, canonical, etc.) as well as of boundary conditions.

To eliminate such dependence, we have to consider an infinite medium, i. e., to take the limit  $V \rightarrow \infty$  first, with  $N/V = n$  fixed as usual, and  $k \rightarrow 0$  second. If, for practical reasons, we want to calculate  $\lim_{k \rightarrow 0} \chi(k)$  by equating it with  $\chi(k=0)$ , we can do so only in an ensemble which allows, even for finite  $V$ , fluctuations of  $N$  as they take place locally, i. e., as if the system enclosed in volume  $V$  were a part of an

much larger system with which it freely exchanges particles (and energy). This, however, is the characteristic property of the grand canonical ensemble.

Eq. (4.27d) is an immediate consequence of the  $f$ -sum rule (3.34) which in turn expresses the equal time commutator

$$[n(\vec{r}), \vec{g}(\vec{r}')] = -i\hbar \vec{\nabla} n(\vec{r}) \delta(\vec{r}-\vec{r}'). \quad (4.34)$$

We only have to use particle conservation,

$$\partial_t n(\vec{r}, t) = -\vec{\nabla} \cdot \vec{g}(\vec{r}, t)/m = -\vec{\nabla} \cdot \vec{g}_z(\vec{r}, t)/m, \quad (4.35a)$$

in the form

$$\omega^2 \chi''_{mn}(k\omega) = k^2 \chi''_z(k\omega)/m^2 \quad (4.35b)$$

to obtain eq. (4.27d) from (3.34). Note that this sum rule holds for arbitrary  $k$ .

For a classical system, the transverse sum rule (4.27e) is also exact for all  $k$ . By the classical fluctuation-dissipation theorem (3.39),

$$\chi_{g_i g_j}(\vec{k}) = \beta \int \frac{d\omega}{2\pi} S_{g_i g_j}(\vec{k}, \omega) = \beta \int d(\vec{r}-\vec{r}') e^{-i\vec{k}(\vec{r}-\vec{r}')} \langle g_i(\vec{r}) g_j(\vec{r}') \rangle. \quad (4.36)$$

Now the classical equilibrium average is easy to calculate. In a canonical or grand canonical ensemble the momenta of different particles are not correlated so that  $\langle p_i^\alpha p_j^\beta \rangle = \delta_{ij} \delta_{\alpha\beta} m/\beta$ . And since, classically, averages over positions and momenta factorize, we obtain

$$\langle g_i(\vec{r}) g_j(\vec{r}') \rangle = \delta_{ij} m n / \beta \delta(\vec{r}-\vec{r}') \quad (\text{classically}), \quad (4.37a)$$

where we have used the explicit expression (4.6) for the densities, and therefore for any  $k$

$$\chi_{g_i g_j}(\vec{k}) = \int \frac{d\omega}{\pi} \chi''_{g_i g_j}(\vec{k}, \omega) / \omega = m n \delta_{ij} \quad (\text{classically}). \quad (4.37b)$$

Quantum-mechanically, the transverse equation (4.27e) holds only in the limit as  $k \rightarrow 0$ . It holds in this limit since for very small  $k$ , or very large wavelength, longitudinal and transverse fluctuations are indistinguishable.

Unless something unforeseen happens. Naturally, it does happen: in superfluid helium, as well as in superconductors, there is macroscopic quantum phase coherence, of which one consequence is the fact that longitudinal and transverse fluctuations are distinct even at infinite wavelength, or more precisely,

$$\lim_{k \rightarrow 0} \int \frac{d\omega}{\pi} \chi''_{\uparrow}(k\omega) / \omega = \rho_n < m n \quad (\text{superfluid}). \quad (4.38)$$

The macroscopic manifestations of this property of superfluids are profound, and chapter 10 will be devoted to their discussion. For now, we return to normal fluids where everything is nice and simple.

#### 4.4 The Hydrodynamic Correlation Functions

We have two representations for the small amplitude relaxation problem: the first, given by eqs. (4.16) and (4.24), is macroscopic, and valid only for small wave vector and frequency; the second, generally given by eqs. (3.14), is microscopically rigorous, for any  $k$  and  $\omega$ . Comparing the two we obtain the limiting, hydrodynamic expressions for the microscopic correlation functions. The simplest of these is the transverse momentum density correlation function  $\chi''_{\uparrow}(k\omega)$ . From (4.16) and (3.14), and using the Kubo function introduced in (3.42-44), we find

$$C_{ij}(kz) = \beta^{-1} \int_{\pi}^{\infty} \frac{d\omega}{\pi} \frac{X_{ij}''(k\omega)}{\omega(\omega-z)} = \frac{\beta^{-1} m n}{z + ik^2 \eta/mn}, \quad (4.39)$$

for  $\text{Im}z > 0$ . And taking the imaginary part at  $z = \omega + i0$ , we obtain

$$\frac{1}{\omega} X_{ij}''(k\omega) = \frac{k^2 \eta}{\omega^2 + (k^2 \eta/mn)^2}. \quad (4.40)$$

This function has, again, the familiar diffusion structure. Note in passing that the shear viscosity,  $\eta$ , must of course be positive; eq. (4.40) proves that since  $\omega X_{ij}''(k\omega) \geq 0$ .

The longitudinal correlation functions follow in the same fashion. Of

course, we do have to invert the matrix in eq. (4.24) now, but for  $k$  so small that

$$(D_T k^2)^2 \ll c^2 k^2, \quad (4.41)$$

that is not so fearsome. For the Kubo functions, we obtain:

$$C_{nm}(kz) = \beta \beta^{-1} n \left( \frac{\partial n}{\partial p} \right)_T \left[ \frac{c}{c} \frac{z + ik^2 (\Gamma + D_T [c/c_p - 1])}{z^2 - c^2 k^2 + izk^2 \Gamma} + (1 - \frac{c}{c_p}) \frac{1}{z + ik^2 D_T} \right], \quad (4.42a)$$

$$C_{qq}(kz) = \frac{\beta \beta^{-1} m n c}{z + ik^2 D_T} \frac{\Gamma}{D_T}, \quad (4.42b)$$

$$C_{nq}(kz) = \beta \beta^{-1} \Gamma \left( \frac{\partial n}{\partial T} \right)_p \left[ \frac{ik^2 D_T}{z^2 - c^2 k^2 + izk^2 \Gamma} + \frac{1}{z + ik^2 D_T} \right]. \quad (4.42c)$$

These expressions are rigorous in the following sense: If the Kubo functions  $C_{ij}(kz)$  are written as a sum of individual pole contributions,

#### 4.4 The Hydrodynamic Correlation Functions

$$C_{ij}(kz) = \beta \beta^{-1} X_{ij}(k) \left[ \frac{Z_{ij}^{(+)}(k)}{z - ck + \frac{1}{2} k^2 \tau} + \frac{Z_{ij}^{(-)}(k)}{z + ck - \frac{1}{2} k^2 \tau} + \frac{Z_{ij}^{(D)}(k)}{z + ik^2 D_T} \right], \quad (4.43)$$

then hydrodynamics correctly determines the positions of the poles to order  $k^2$ , the residues  $Z_{ij}$  to order  $k$ . Note that all the non-vanishing susceptibilities are in  $k$ , so that e.g.,  $X_{nm}(k) = n \left( \frac{\partial n}{\partial p} \right)_T + O(k^2)$ .

From eqs. (4.42), we obtain the absorptive parts  $X''(k\omega)$  easily:

$$\frac{1}{\omega} X_{nm}''(k\omega) = n \left( \frac{\partial n}{\partial p} \right)_T \left[ \frac{(c/c_p)^2 c^2 k^4 \Gamma}{(\omega^2 - c^2 k^2)^2 + (\omega k \Gamma)^2} + \frac{(1 - c/c_p) k^2 D_T}{\omega^2 + (k^2 D_T)^2} - (1 - \frac{c}{c_p}) \frac{(\omega^2 - c^2 k^2) k^2 D_T}{(\omega^2 - c^2 k^2)^2 + (\omega k \Gamma)^2} \right], \quad (4.44)$$

$$\frac{1}{\omega} X_{qq}''(k\omega) = m n c \frac{\Gamma}{D_T} \frac{k^2 D_T}{\omega^2 + (k^2 D_T)^2}, \quad (4.45)$$

$$\frac{1}{\omega} X_{nq}''(k\omega) = \Gamma \left( \frac{\partial n}{\partial T} \right)_p \left[ \frac{k^2 D_T}{\omega^2 - c^2 k^2 + (\omega k \Gamma)^2} - \frac{(\omega^2 - c^2 k^2) k^2 D_T}{(\omega^2 - c^2 k^2)^2 + (\omega k \Gamma)^2} \right]. \quad (4.46)$$

After this onslaught, the reader will appreciate that density correlation functions do indeed have a very complicated analytic structure at hydrodynamically small  $\omega$  and  $w$ . We have not written down correlation functions which involve the longitudinal momentum density  $g_z$  since for any  $A$ ,

$$\omega X_{nA}''(k\omega) = \frac{1}{m} k X_{g_A}''(k\omega) \quad (4.47)$$

because of particle conservation.

Now let us try to understand what we have obtained. There are two processes, one propagating and one diffusive. To order  $k$ , the diffusive mode corresponds to fluctuations of the entropy variable  $q(\vec{r}, t) = \epsilon(\vec{r}, t) - \frac{c \cdot \vec{p}}{n} n(\vec{r}, t)$ . As is apparent from eq. (4.44b), a local entropy fluctuation will spread out by a random walk process, with diffusivity  $D_T = \kappa / mnc$ . Only at very low temperature, when  $(\frac{\partial T}{\partial n})_S = 0$ , is the diffusive mode a pure temperature fluctuation, see eq. (4.20b).

The other modes are, of course, identical with sound waves, propagating with the Laplacean speed of sound  $c = (\frac{\partial p}{\partial m})_S^{1/2}$ . Their damping is viscous, as seen from eq. (4.25d), but contains a thermal admixture  $\sim \kappa$  as well. Only at very low temperature, when  $c_p \approx c_v$ , is the propagating mode a purely mechanical density fluctuation.

The discrepancy between the Newtonian, isothermal, speed of sound  $c_N = (\frac{\partial p}{\partial m})_T^{1/2}$  and the observed adiabatic one  $c = (\frac{\partial p}{\partial m})_S^{1/2}$  is interesting.

Historically, Newton's theory, which was purely mechanical, could only be corrected with the later recognition of thermal—as different from mechanical—processes. It is the coupling of density and energy fluctuations which converts  $c_N$  to  $c$ . In simple microscopic theories, such coupling is often omitted, and the isothermal speed of sound obtained. As an interesting exercise, the reader may amuse himself by repeating the calculation which led us to eq. (2.107), applying the same reasoning to the particle density instead of the magnetization. He will find the dispersion relation  $\omega = c_N k + O(k^2)$ : high-frequency sound is isothermal.

The contrast in complexity between, say,  $X_{nn}''$  and  $X_1''$  is striking. The transverse momentum density is conserved, and not coupled to any other conserved quantity. This fact results in its simple diffusion structure. The density variable and its correlation function are complicated by two features: First, its current, the longitudinal momentum density, is itself conserved because of this, a density

fluctuation can "overshoot" and come to equilibrium in an oscillatory (propagating) rather than a diffusive fashion. And second, the density is coupled to yet another conserved variable, the energy density.

The last term in (4.44a) is of only minor importance as far as light scattering experiments are concerned, and it is often omitted. However, in order for  $X_{nn}''(k, \omega)$  to satisfy the  $f$ -sum rule (3.34), and therefore to be in accord with momentum conservation, this term is necessary. In addition, the hydrodynamic expressions (4.44) exhaust all the thermodynamic sum rules (4.27). This is no surprise; our derivation guarantees that these sum rules are obeyed, to order  $k$ . However, none of the higher sum rules, such as  $\int dx^3 X''$ , can be fulfilled. This is in direct parallel to our discussion in section 2.10; the hydrodynamic correlation functions are rigorous at small  $k$  and  $\omega$ , but they fall off too slowly at large frequency.

#### 4.5 Light Scattering

Eq. (4.44a) is an old and famous result which has been first derived by Landau and Placzek (1934). Its experimental importance is, of course, the fact that  $X_{nn}''(k, \omega)$ , or rather

$$S_{nn}(k, \omega) = 2\hbar(1 - e^{-\hbar\omega/\beta})^{-1} X_{nn}''(k, \omega) \approx 2k_B T X_{nn}''(k, \omega) / \omega, \quad (4.46)$$

is what is measured in (many) light scattering experiments, see eq. (4.3). (With  $\omega$  of order  $ck$  where  $c \approx 10^5$  cms $^{-1}$  say and  $k \approx 10^4$  cm $^{-1}$ ,  $2\hbar(1 - e^{-\hbar\omega/\beta})^{-1} = 2/\beta\omega$  for reachable temperatures.) Indeed, since  $k = 2k_B \sin(\theta/2)$  is maximally  $k_{\max} \approx 2k_B \approx 10^{-4}$  cm $^{-1}$ ,  $k$  is much smaller than the inverse mean free path in liquids and in all but very dilute gases.  $\omega$  is also small, of order  $10^9$  s $^{-1}$  or less, so that our hydrodynamic theory should be perfectly appropriate. And light scattering experi-

ments produce a wealth of information.

To see this, consider Fig. 4.3 which gives the spectrum in some detail.

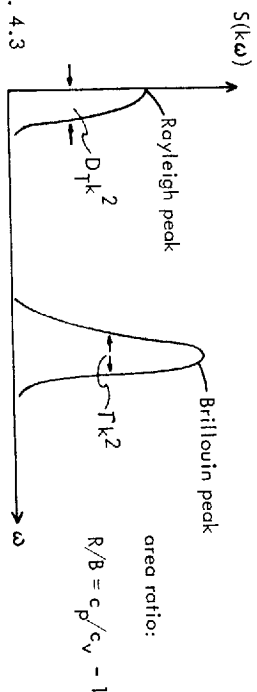


Fig. 4.3

The most immediate quantities to obtain are the speed of sound, from the position of the Brillouin line, the sound attenuation constant  $\Gamma$  from its width, and the thermal diffusivity from the width of the central peak. To measure the isothermal compressibility  $(\partial n/\partial p)_T$  or the specific heat ratio  $c_p/c_v = mc^2(\partial n/\partial p)_T$  seems to require the sum rule (4.27d) and therefore an absolute intensity measurement. Such measurements are difficult, and accurate knowledge of the "factors" in eq. (4.3), in particular the polarizability contained in them, is hard to come by. Fortunately, relative intensity measurements suffice to obtain  $c_p/c_v$  since the ratio (called the Landau-Placzek ratio) of the areas under half the Rayleigh peak and one Brillouin peak is  $\frac{c_p}{c_v} - 1$ . The reader will convince himself of this fact from eq. (4.44d) or, much more easily, by looking at the residues in eq. (4.42a). In summary then, one obtains from Brillouin and Rayleigh scattering these quantities:

$$\frac{c_p}{c_v}; \left(\frac{\partial p}{\partial m n}\right)_T; D_T = \frac{\kappa}{mnc}; D_L = \left(\frac{4}{3}n + 5\right)/mn. \quad (4.47)$$

Quite a harvest. Note, however, what these experiments involve. The frequency shifts  $\omega$ , of order  $ck$ , are extremely small,  $\leq 10^8 \text{ s}^{-1}$  which is to be compared to  $\sim 10^{15} \text{ s}^{-1}$  for the frequency of the incident light. This requires light sources which are extremely monochromatic; lasers, in other words. It also requires very accurate measurements of frequency shifts which is accomplished by self-beating

#### 4.5. Light Scattering

techniques, specially invented to owe the theoretician.

Suppose we could extend these measurements of  $X''_{nm}(k\omega)$  or  $S_{nm}(k\omega)$  to arbitrary  $k$  and  $\omega$ . Through X-ray and neutron scattering, and through the computer studies of molecular dynamics which are a theoretician's experiment (see the brief review of Berne and Forster, 1971), one can go at least part of the way. What would we get? Well, knowing the particle mass  $m$  we could, even from the hydrodynamic spectrum, obtain the mass density  $n$  because of the  $f$ -sum rule

$$\int d\omega (\omega/\pi) \omega X''_{nm}(k\omega) = k^2 (n/m). \quad \text{Moreover, we can obtain the static structure factor } S(k) \equiv S_{nm}(k, \omega=0) \text{ since} \quad (4.48)$$

$$S(k) = k_B T \int \frac{d\omega}{\pi} X''_{nm}(k\omega)/\omega,$$

where we have taken a classical system. If we know the interaction potential  $\psi(r)$  this determines the pressure and the energy. Namely, from the eqs. (4.6), we find that

$$e = \frac{3}{2} n k_B T + \frac{1}{2} n^2 \int d\mathbf{r} \mathbf{r} \psi(r) g(r), \quad (4.49)$$

$$p = n k_B T - \frac{1}{6} n^2 \int d\mathbf{r} \mathbf{r} \cdot \mathbf{r} \psi(r) g(r), \quad (4.50)$$

where  $g(r)$  is the pair correlation function,

$$n^2 g(|\mathbf{r}-\mathbf{r}'|) = \langle \sum_{\alpha \neq \beta} \delta(\mathbf{r}-\mathbf{r}'_{\alpha}) \delta(\mathbf{r}'-\mathbf{r}'_{\beta}) \rangle$$

$$= n^2 + \int \frac{d\mathbf{k}}{(2\pi)^3} e^{i\mathbf{k}(\mathbf{r}-\mathbf{r}')} [S(k) - n], \quad (4.51)$$

and  $\mathbf{v}'(r) = \frac{d\mathbf{v}(r)}{dr}$ . From  $e$  in particular, we could obtain the specific heat,  $mnc_v = (\partial e/\partial T)_n$ . A theoretician should therefore calculate  $X''_{nm}$ , or better the momentum density correlation function  $X''_{g_i g_j}$  since its transverse part  $X''_{g_i g_j}$  determin-

the shear viscosity  $\eta$ . From  $X_{9,9}''(ku)$  he would get all the thermodynamic and hydrodynamic parameters in a classical system, and most of them in a quantum system.

Let us mention, finally, the special features that appear when the liquid is near its critical point where  $(\partial\rho/\partial\eta)_T \rightarrow 0$ . There are three effects. First, the total light scattering intensity becomes enormous because of the thermodynamic sum rule (4.27a). This is the phenomenon of critical opalescence. Second, while at low temperatures the Brillouin peaks are much more prominent than the central peak since  $c_p \approx c_v$ , near the critical point the Landau-Placzek ratio  $\frac{c_p}{c_v} - 1$  becomes very large since

$$c_p - c_v = \frac{T}{m n} \left( \frac{\partial \rho^2}{\partial T} \right)_n \left( \frac{\partial \rho}{\partial p} \right)_T \rightarrow \infty. \quad (4.52)$$

Therefore, most of the intensity near the critical point is in the central peak.

The entropy fluctuates wildly while the more mechanical sound waves are essentially unaffected which is physically as one should expect. Third, even though the total Rayleigh intensity increases, its spectral width becomes very narrow since  $D_T = \kappa/\rho mc_p$  and  $c_p \rightarrow \infty$ . This is the phenomenon of critical slowing down already encountered in section 2.10.  $10^{-2}$  degrees away from the critical point, you can, after each change of temperature, go to the movies while the system slowly comes to equilibrium.

As explained in section 2.10, the transport coefficient, which is here  $\kappa$ , is determined by local, rapid fluctuations and should be insensitive to the large-scale rearrangement that goes on at the critical point. This argument, implicit in the early theory by Van Hove (1954), is qualitatively borne out:  $\kappa/c_p \rightarrow \infty$  at  $T_c$ . More recently, however, it has been found that  $\kappa$  becomes weakly singular as well. The experimental and theoretical situation in critical phenomena is reviewed in the book by Stanley (1971). This has been field of continued intensive activity

since Wilson's (1971) renormalization group ideas appeared; another book would already be necessary to describe it. (It is being written: Ma, 1975).

#### 4.6 Kubo Expressions for the Transport Coefficients

From the results we have obtained, eqs. (4.44), we can extract the transport coefficients by performing appropriate limits. The limits involved are those for small  $k$  and  $\omega$  where the hydrodynamic theory becomes rigorous. The Kubo-type relations which we obtain are therefore exact expressions, relating macroscopic measurements (of  $\eta$ ,  $\kappa$  etc.) to the underlying microscopic structure.

From eq. (4.40), we obtain the shear viscosity as

$$\eta = \lim_{\omega \rightarrow 0} \left[ \lim_{k \rightarrow 0} \frac{1}{k} X_1''(k, \omega) \right]. \quad (4.53a)$$

The longitudinal viscosity follows similarly from (4.44a) as

$$\frac{4}{3} \eta + \zeta = \lim_{\omega \rightarrow 0} \left[ \lim_{k \rightarrow 0} \frac{m}{k} \frac{\omega^2}{4} X_{nn}''(k, \omega) \right] = \lim_{\omega \rightarrow 0} \left[ \lim_{k \rightarrow 0} \frac{\omega}{k} X_2''(k, \omega) \right], \quad (4.53b)$$

since  $m^2 \omega^2 X_{nn}''(k, \omega) = k^2 X_2''(k, \omega)$  from particle conservation, see eq. (4.45). And finally, the entropy correlation function (4.44b) gives the heat conductivity,

$$\kappa T = \lim_{\omega \rightarrow 0} \left[ \lim_{k \rightarrow 0} \frac{\omega}{k} X_{qq}''(k, \omega) \right]. \quad (4.53c)$$

Thus all three transport coefficients involved in the hydrodynamics of a normal liquid are given by expressions of the same structure we already encountered in eq. (2.57), namely

$$\lambda_{AB} = \lim_{\omega \rightarrow 0} \left[ \lim_{k \rightarrow 0} \frac{\omega}{k} X_{AB}''(k, \omega) \right] \quad (4.54)$$

for the transport coefficient  $\lambda_{AB}$  associated with the conserved variables A, B. As it happens, the normal liquid has only diagonal  $\lambda$ 's.  $\lambda_{AB}$  would appear in constitutive relations in the form

$$6\langle \dot{f}_A^{\vec{r},t} \rangle = -\lambda_{AB} \nabla \delta b(\vec{r},t), \tag{4.55}$$

where  $\delta b$  is the thermodynamic force conjugate to the variable  $6\langle A \rangle$ :

$\delta b_n = \delta p/n$ ,  $\delta b_q = \delta T/T$  etc., as we will see more systematically later; see also Martin (1965). The current densities are defined by

$$\partial_t A(\vec{r},t) + v_1^A \dot{f}_1^A(\vec{r},t) = 0 \quad \text{and} \quad \partial_t B(\vec{r},t) + v_1^B \dot{f}_1^B(\vec{r},t) = 0. \tag{4.56}$$

Note that  $\chi_{AB}''(k\omega) = \chi_{BA}''(k\omega)$  if A and B have the same signature under time reversal and parity. Then

$$\lambda_{AB} = \lambda_{BA}, \tag{4.57}$$

which are the famous Onsager relations.

If we use the conservation laws (4.56) and the fluctuation-dissipation theorem (3.38), we can express the transport coefficients in terms of current correlations, as we did in eq. (2.29a). Generally, we obtain from (4.54)

$$\lambda_{AB} = \lim_{\omega \rightarrow 0} \lim_{k \rightarrow 0} \frac{1}{4kT} \int_{-\infty}^{\infty} dt \int d\vec{r} e^{i\omega t - ik \cdot \vec{r}} \langle \dot{f}_2^A(\vec{r},t), \dot{f}_2^B(\vec{0},0) \rangle, \tag{4.58}$$

where  $\dot{f}_2 = \vec{k} \cdot \dot{\vec{f}}$  is the longitudinal component of the current density. (There is no need to subtract the constant terms  $\langle \dot{f}^A \rangle \langle \dot{f}^B \rangle$  as in (3.37) since their Fourier transform is  $\sim \delta(\omega)$  and does not contribute to the limit as  $\omega \rightarrow 0$ .) This procedure, and a pinch of rotational symmetry, gives the hydrodynamic transport coefficients in the invariant form

4.6 Kubo Expressions for the Transport Coefficients

$$\kappa_T = \lim_{\omega \rightarrow 0} \lim_{k \rightarrow 0} \frac{1}{12kT} \int_{-\infty}^{\infty} dt \int d\vec{r} e^{i\omega t - ik \cdot \vec{r}} \langle \dot{f}_1^q(\vec{r},t), \dot{f}_1^q(\vec{0},0) \rangle, \tag{4.59a}$$

$$\eta(\zeta) = \lim_{\omega \rightarrow 0} \lim_{k \rightarrow 0} \frac{1}{4kT} \int_{-\infty}^{\infty} dt \int d\vec{r} e^{i\omega t - ik \cdot \vec{r}} \left( \frac{1}{3} \frac{k_i k_j}{k} + \zeta \frac{k_i k_j}{k^2} \right) \langle \tau_{im}^{\vec{r},t}, \tau_{jn}^{\vec{0},0} \rangle. \tag{4.59b}$$

These results make it evident that not only  $\kappa$ ,  $\eta$  and  $\zeta$ , but also  $\zeta$  are positive expressions, aren't they? They invite a few comments of a general nature:

Consider eq. (4.58), expressing a transport coefficient in terms of current densities of conserved variables. These currents (i. e.,  $\tau_{ij}^A, \dot{f}_j^A$ ) are not, in general, themselves conserved. Consequently, fluctuations of the total current  $\dot{f}^A(t) = \int d\vec{r} \dot{f}^A(\vec{r},t)$  will decay within a finite, microscopic time, as explained in section 2.1. In the absence of long-ranged correlations, the correlation function in (4.58) will therefore be different from zero, effectively, only over some finite range of  $\vec{r}$  and  $t$ . There is thus no convergence problem with the integral

$$\lambda_{AB} = \frac{1}{kT} \int_{-\infty}^{\infty} dt \int d\vec{r} \left[ \frac{1}{2} \langle \dot{f}_2^A(\vec{r},t), \dot{f}_2^B(\vec{0},0) \rangle - \langle \dot{f}_2^A \rangle \langle \dot{f}_2^B \rangle \right], \tag{4.60}$$

and a finite transport coefficient results. What we have just said is that the limit (4.54) will, in general, be finite if A and B are conserved but  $\dot{f}^A$  and  $\dot{f}^B$  are not.

Now the longitudinal momentum density  $g_{\vec{k}}(\vec{r},t)$  is the current of the conserved mass density  $m(\vec{r},t)$ . However,  $g_{\vec{k}}$  obeys itself a continuity equation with the current  $\tau_{zz}$ , taking  $\vec{k} = k\hat{z}$ . According to the argument given above, zz-component of (4.59b) which gives  $\frac{4}{3} \eta + \zeta$ , should thus converge, and follow the equations backwards to (4.59b) this means that for small but finite  $\omega$



$\lim(k \rightarrow 0) k^{-4} X_{nn}''(k; \omega)$  must be finite. Consequently,  $\lim(k \rightarrow 0) k^{-2} X_{nn}''(k; \omega)$  vanishes, and therefore

$$\lambda_{nn} = \lim_{\omega \rightarrow 0} \left[ \lim_{k \rightarrow 0} \frac{\omega}{k} X_{nn}''(k; \omega) \right] = 0. \quad (4.61)$$

By the same token,

$$\lambda_{nq} = \lim_{\omega \rightarrow 0} \left[ \lim_{k \rightarrow 0} \frac{\omega}{k} X_{nq}''(k; \omega) \right] = 0. \quad (4.62)$$

These coefficients would appear in constitutive relations in the form already given in eqs. (4.11). We have now given the answer promised there. Since we omitted the coefficients  $\lambda_{nn}$  and  $\lambda_{nq}$  from the outset, it is hardly startling that our expressions (4.44) are in agreement with eqs. (4.61) and (4.62).

It is apparent from (4.61) and (4.62) that

$$\lim_{k \rightarrow 0} \frac{1}{k} X_{qq}''(k; \omega) = \lim_{k \rightarrow 0} \frac{1}{k} X_{q+\lambda n, q+\lambda n}''(k; \omega), \quad (4.63)$$

whatever  $\lambda$ . If we choose  $\lambda = (c+p)/n$  and remember that  $\delta q + \frac{c+p}{n} \delta n = \delta \epsilon$ , eq. (4.19), we find that the Kubo expression for the heat conductivity can also be written in terms of the energy-energy correlation function,

$$\kappa T = \lim_{\omega \rightarrow 0} \left[ \lim_{k \rightarrow 0} \frac{\omega}{k} X_{\epsilon\epsilon}''(k; \omega) \right] \quad (4.64)$$

instead of eq. (4.53c). This fact, a consequence as we saw of momentum conservation, is given a thorough analysis by Kadonoff and Martin (1963, p. 458) which we urge our reader to look up, even if it means that he might become aware of just how much we have pillaged from this fundamental paper.

#### 4.7 Free Particle Behavior

The expressions for correlation functions which we have obtained in the last few sections, are asymptotically rigorous. They hold in the hydrodynamic regime when the system, as a result of many collisions, has reached local equilibrium. In terms of frequency and wave vector, they hold when  $k\ell \ll 1$  and  $\omega\tau \ll 1$  where  $\ell$  is the mean free path of a particle, and  $\tau$  the mean collision time. In a dense liquid, this region is large: the mean free path is of the order of the atomic force range, a few Angstroms maybe, and the collision time, by the dimensional argument that led to (2.12), is also very small except at the lowest temperatures where most liquids freeze. In a gas, the range of validity of the hydrodynamic expressions shrinks as  $\ell$  and  $\tau$  are much larger than in a liquid.

At the extreme other end is the simple gas of non-interacting point particles. It may be worthwhile to write down a few expressions for this simple system for comparison. The free classical gas is particularly simple. Since the equations of motion are  $r^{\alpha\alpha}(\dot{t}) = r^{\alpha\alpha}(0) + (p^{\alpha\alpha}/m)t$  and  $\dot{p}^{\alpha\alpha}(t) = p^{\alpha\alpha}(0)$  for the  $\alpha$ -th particle, one shows easily that

$$X_{nn}''(k; \omega) = \sqrt{\pi/2} \frac{n}{m v_0} \left( \frac{\omega}{k} \right)^2 e^{-\frac{1}{2} \left( \frac{\omega}{v_0 k} \right)^2} \quad (4.65a)$$

and

$$X_{\dot{t}}''(k; \omega) = \sqrt{\pi/2} \frac{1}{m n} \left( \frac{\omega}{k} \right)^2 e^{-\frac{1}{2} \left( \frac{\omega}{v_0 k} \right)^2}, \quad (4.65b)$$

where  $v_0 = (m\beta)^{-1/2}$  is the thermal velocity. The corresponding expressions for the non-interacting Fermi gas are somewhat more complicated, and shall not be given here (see, for example, Nozières 1964).

It is interesting, though not too significant, that the transport coefficients vanish. For example, the Kubo expressions (4.58) and eqs. (4.65) give

$\eta = 0$  and  $\zeta = 0$  since  $\lim_{k \rightarrow 0} k^{-3} e^{-\alpha/k^2} = 0$  for  $\alpha > 0$ ; similarly, the heat conductivity  $\kappa$  vanishes. Operationally, of course, transport coefficients cannot even be defined for a gas of non-interacting particles. A measurement of the heat conductivity, for example, is only possible if we can apply, quasi-statically, a temperature gradient and maintain it while we measure the heat current. However, only for a system with a finite mean free path can a temperature gradient be maintained quasi-statically. A free gas would "run away", and the standard measurements of transport coefficients cannot be performed. Still, it may be satisfying for some that in this case the Kubo expressions give the most sensible result: zero.

#### 4.8 Sum Rule Calculations

In this section, we will attempt to extend our results, eqs. (4.40) and (4.44), from the collision-dominated regime of hydrodynamics to larger frequency and wavenumber. The purpose of this enterprise is twofold. Those rapid microscopic processes which decay over short times, of the order of the collision time  $\tau$ , are contained in eqs. (4.40) and (4.44) in a summary fashion; they determine the numerical values of the transport coefficients. If one wants to calculate these coefficients, one has to obtain more information about high frequency processes. Moreover, their spectrum can be obtained directly in some cases, for example by neutron scattering.

Now we can obtain at least some information about the short time behavior of correlation functions from their frequency moments. In sections 2.9 and 3.4 we showed how sum rules can be calculated, in principle and sometimes in practice. Let us consider the transverse momentum density correlation function,  $\chi_{\perp}''(k, \omega)$ . According to eq. (3.33), its moments,

#### 4.8 Sum Rule Calculations

$$\langle \omega_{\perp}^{\nu} \rangle \equiv \frac{1}{m\Omega} \int_{-\pi}^{\pi} d\omega \omega^{\nu} \chi_{\perp}''(k, \omega) / \omega, \quad (4.66)$$

are determined in terms of multiple commutators (Poisson brackets classically) with the Hamiltonian. For a classical system with the Hamiltonian (4.5), one obtains (Forster, Martin, and Yip 1968)

$$\beta m \langle \omega_{\perp}^2 \rangle = k^2 + n\beta \int d\vec{r} g(r) (1 - \cos \vec{k} \cdot \vec{r}) \frac{1}{2} [\nabla^2 - (\vec{k} \cdot \nabla)^2] v(r), \quad (4.67)$$

$$\beta^2 m^2 \langle \omega_{\perp}^4 \rangle =$$

$$3k^4 + 3n\beta \int d\vec{r} g(r) \left\{ k^2 \nabla^2 v - \frac{2}{3} (\vec{k} \cdot \nabla)^2 v \right.$$

$$\left. + \sin \vec{k} \cdot \vec{r} [\nabla^2 - (\vec{k} \cdot \nabla)^2] (\vec{k} \cdot \nabla) v + \frac{1}{3} \beta (1 - \cos \vec{k} \cdot \vec{r}) [\nabla^2 \nabla^2] - (\vec{k} \cdot \nabla \nabla^2 v)^2 \right\}$$

$$+ \frac{1}{2} n^2 \beta^2 \int d\vec{r} \int d\vec{r}' g(r, r') \left\{ 1 + \cos [\vec{k} \cdot (\vec{r} - \vec{r}')] - 2 \cos \vec{k} \cdot \vec{r} \right\}$$

$$\times [(\vec{\nabla} \cdot \nabla')^2 - (\vec{k} \cdot \nabla)(\vec{k} \cdot \nabla')] v(r'), \quad (4.68)$$

where  $\vec{k} = \vec{k}'/k$ . These expressions are frightening, and higher order moments would become more horrible yet. They have been given here partly to demonstrate that fact. Still, the two sum rules given are integrals that can be evaluated numerically if the interparticle potential  $v(r)$  is known, and in addition two static correlation functions: the famous pair correlation function  $g(r)$ , already introduced in (4.51), which gives the probability of finding a particle at point  $\vec{r}$  if we know that there is one at the origin; and the triplet correlation function which is defined by

$$n^3 g_3(\vec{r}, \vec{r}') = \sum_{\alpha \neq \beta \neq \gamma} \langle \delta(\vec{r} - \vec{r}^{\alpha}) \delta(\vec{r}' - \vec{r}^{\beta}) \delta(\vec{r}'') \rangle. \quad (4.69)$$

Information about these functions can be obtained from the numerical computer calculations of molecular dynamics. (For a recent review, see e.g. Berne and

Forster 1971). In these studies, the most frequently used potential is the Lennard-Jones (6-12) potential

$$v(r) = 4\epsilon\left[\left(\frac{r}{\sigma}\right)^{12} - \left(\frac{r}{\sigma}\right)^6\right], \tag{4.70}$$

which is appropriate for the noble gases. For argon, for example,  $\epsilon = 120^\circ\text{K}$  and  $\sigma = 3.4 \text{ \AA}$ . For this system therefore, it is feasible to compute the sum rules (4.67) and (4.68). Numerical data for  $\langle u_{\dagger}^2 \rangle$  and  $\langle u_{\dagger}^4 \rangle$ , near  $k = 0$  are given in Forster et al. (1968), for a range of densities and temperatures. So let us now consider the moments  $\langle u_{\dagger}^2 \rangle$  and  $\langle u_{\dagger}^4 \rangle$  as known. What do we do with them?

4.8.1. High Frequency Shear Waves

The answer is contained in the work we did in sections 2.10 and 2.11.

The hydrodynamic expression for  $\chi_{\dagger}''(k, \omega)$ , eq. (4.40), is not compatible with the sum rules; it has to be generalized. Now the proof of eq. (2.94), given earlier for the magnetic correlation function, applies to  $\chi_{\dagger}''(k, \omega)$  as well. In other words, in terms of a real function  $D_{\dagger}'(k, \omega)$  which is positive, even in  $\omega$ , and has the complex Hilbert transform

$$D_{\dagger}(k, z) = \int \frac{d\omega}{2\pi i} \frac{D_{\dagger}'(k, \omega)}{\omega - z}, \tag{4.71}$$

we can always write the rigorous dispersion relation

$$C_{\dagger}(k, z) = \frac{i\beta^{-1} m n}{z + ik^2} D_{\dagger}'(k, z), \tag{4.72}$$

which is the complete analogue of (2.94). Comparison with eq. (4.39) shows that (4.72) can be understood as a generalization of the hydrodynamic result, to account for a frequency and wave number dependent viscosity

$$\eta(k, z) = m n D_{\dagger}'(k, z). \tag{4.73}$$

Eq. (4.73) has therefore been called the basic equation of "Generalized Hydrodynamics", for the transverse case.

Let us first jump from extremely low to asymptotically high frequencies.

We noted in section 2.10 that to accommodate finite sum rules for  $\chi_{\dagger}''(k, \omega)$ , the function  $D_{\dagger}'(k, \omega)$  has to have finite frequency moments. And using our earlier method, expansion in terms of  $1/z$ , we find that its zeroth moment is given by

$$c_{\dagger 00}^2(k) \equiv \int \frac{d\omega}{2\pi} D_{\dagger}'(k, \omega) = \langle y_{\dagger}^2(k) \rangle / k^2. \tag{4.74}$$

For very high frequencies therefore where  $D_{\dagger}(z) \approx \frac{i}{z} c_{\dagger 00}^2$ , we obtain from (4.72) the asymptotic result

$$C_{\dagger}(k, z) \approx \frac{i z \beta^{-1} m n}{z - k^2} c_{\dagger 00}^2(k). \tag{4.75}$$

Again, as in (2.107), we find reactive behavior at high frequency. There are shear waves, with a speed which at small  $k$  is obtained from (4.67) in the form

$$\beta m c_{\dagger 00}^2(0) = 1 + \frac{2\pi}{15} n \beta \int_0^{\infty} dr g(r) \frac{d}{dr} \left[ r^4 \frac{dv(r)}{dr} \right]. \tag{4.76}$$

This result has first been obtained by Zwanzig and Mountain (1965) who identified the quantity  $G_{\infty} = m n c_{\dagger 00}^2(0)$  as the high-frequency shear modulus. It describes the initial elastic response of the fluid to a suddenly applied shear force. Indeed, since the microscopic expressions for the energy density  $\epsilon$  and the pressure  $p$ , namely eqs. (4.49, 50), are similar to (4.76), one can, for the case of the (6-12) potential (4.70), express  $G_{\infty}$  in terms of  $\epsilon$  and  $p$ . The result,

$$G_{\infty} = \frac{26}{5} n k_B T + 3p - \frac{24}{5} \epsilon, \tag{4.77}$$

has been discussed by Zwanzig and Mountain in numerical detail. A similar and instructive quantum-mechanical calculation which is applicable to liquid Helium, has been given by Puff (1965).

#### 4.8.2 Interpolation Ansatz

We now have a low-frequency result in (4.39) and a high-frequency result in (4.75). Can we close the gap? Naturally, one must not be immodest: only a detailed microscopic calculation could accomplish this goal. In a rare gas, such a calculation might be feasible if laborious since the Boltzmann equation gives a rather detailed picture of the dynamics. (For related work, see e.g., Mazenko, Wei, and Yip 1972, and references given there.) For a liquid, the problem is infinitely more difficult (see Rice and Gray 1965). On the other hand, the gap between "low" and "high" frequencies in a simple liquid is not all that large since the mean free path and the collision time are small. We can therefore hope for good luck with a relatively simple, and more or less ad hoc, interpolation model.

Again, we utilize the general representation (4.72), in the spirit of our work in section 2.10. We do not know the function  $D'(k\omega)$ , of course, but we can hope to get by with a simple ansatz. The ansatz function  $D'(k\omega)$  should be even and positive, of course. It also should fall off rapidly at large  $\omega$  so that its frequency moments exist. Indeed, if we choose a  $D'(k\omega)$  which fulfills the sum rule (4.74) (and therefore (4.67)), we will guarantee the correct behavior (4.75) at high frequencies. At small  $\omega$  and  $k$ ,  $D'(k\omega)$  should be a smooth function of these variables, essentially a constant. The representation (4.72) would then reproduce the correct hydrodynamic behavior in this region, with the shear viscosity given by

$$\eta = mn D'_+(0,0) = \frac{1}{2} mn D'_+(0,0). \quad (4.78)$$

#### 4.8 Sum Rule Calculations

And so let us be courageous, and try a Gaussian ansatz function

$$D'_+(k\omega) = 2 c_{1\infty}^2(k) \tau(k) e^{-(\omega\tau(k))^2/\pi}, \quad (4.79)$$

which is in accord with all the restrictions given above. If we use (4.78) to determine the parameter  $\tau(k)$  at small  $k$  in terms of the experimental viscosity, i.e. use

$$\eta = mn c_{1\infty}^2(0) \tau(0) = G_{\infty} \tau(0), \quad (4.80)$$

(4.79) provides an interpolation model for small  $k$  that has at least a good chance of success.

Of course, one must not take the detailed frequency dependence of  $D'_+(k\omega)$  too seriously. A much more modest and very successful, use of this procedure is to obtain a semi-microscopic, parameter-free calculation of the viscosity itself. We have at our avail another bit of knowledge, namely the as yet unused sum rule (4.68). It translates into a second sum rule for  $D'_+(k\omega)$ , namely

$$\int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \omega^2 D'_+(k\omega) = \langle w_1^4(k) \rangle k^{-2} - k^2 c_{1\infty}^2(k). \quad (4.81)$$

Computing this integral from (4.79), we can express  $\tau(k)$  in terms of  $\langle w_1^4(k) \rangle k^{-2}$  and  $c_{1\infty}^2(k)$  both of which have finite limits as  $k \rightarrow 0$ . Eq. (4.80) therefore gives the final result

$$\eta/mn = \frac{1}{2} \frac{1}{\pi} \lim_{k \rightarrow 0} c_{1\infty}^3(k) [\langle w_1^4(k) \rangle k^{-2}]^{-1/2}. \quad (4.82)$$

This simple calculation is remarkably successful. Numerical results, and a comparison with experimental viscosity data, are given in Forster et al. (1968b).

Methods similar to those used in this section can be applied to a wide

variety of fluctuation phenomena. Closely related techniques have been used, for example, by Chung and Yip (1969) to discuss density fluctuations in the neutron scattering region, as well as several other fluctuations in simple liquids.

## CHAPTER 5

### THE MEMORY FUNCTION FORMALISM

One of the most fundamental notions in the theory of interacting many-particle systems is that (almost) nothing that is physically interesting, can be calculated rigorously from first principles. Once this has been recognized -- sometime within the first year of graduate study -- it becomes of crucial importance for those not inclined to give up to hide their partial ignorance of complicated details away in places where it is least likely to cause harm. Abstract and general results or formulations are useful if they indicate how this should be done, if they suggest which objects of the theory, while unknown in detail, are likely to be insensitive to many of the complicated and uncalculable features of the dynamics; if they indicate, in other words, where one may approximate, parametrize, or fudge with relative impunity.

A prime example of this kind of general result is the dispersion relation (2.101) for the spin density correlation function, or its fluid mechanics equivalent (4.72). By itself it is general, rigorous -- and almost empty. If however as we believe, and as we will explain in section 5.4 below, there is an indication that the memory function  $D(kz)$  contains, in its spectrum, neither very low nor extremely high frequencies, the dispersion relation becomes extremely useful: even though the function  $D(kz)$  contains nearly the full horrendous complexity of the many-body problem, at low frequency and wave vector it varies slowly, and can be replaced by a constant: the simple and experimentally interesting hydrodynamic expressions