

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 He³. (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 μ 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 α -th particle has the position $\vec{r}^\alpha(t)$ at time t and the spin s^α which is either $1/2$ or $-1/2$. The δ -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^α 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}^α is the momentum of the α -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

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

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.

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

and a Laplace transformation in time,

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

\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

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

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

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

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

$$\tau(k) = 1/Dk^2 \tag{2.11}$$

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 τ_c which is determined by the microscopic interactions. For a system of classical particles of mass m , inter-

2.1 Hydrodynamic Description

acting with a pair potential of strength ϵ and range a , dimensional arguments suggest that τ_c is of the order

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

which for Helium would give $\tau_c \approx 10^{-12}$ sec. Even though, in a quantum liquid like He³ at low temperatures, the Pauli principle severely restricts the number of decay channels--dimensionally, the small thermal energy $k_B T$ and τ_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

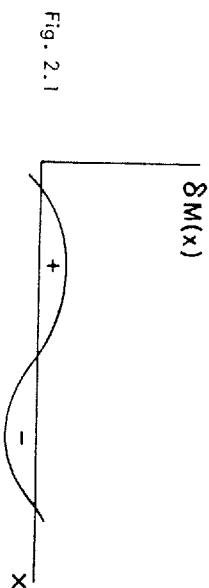


Fig. 2.1

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

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

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

$$\tilde{S}(kz) = \int_{\mathcal{C}} \frac{dx}{2\pi i} \frac{S(k; x)}{x - z}, \quad (2.17)$$

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 ϵ 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 χ ,

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

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 ω 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 ω^{-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 ω 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 ω . 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

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

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 ϵ_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 ω) 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

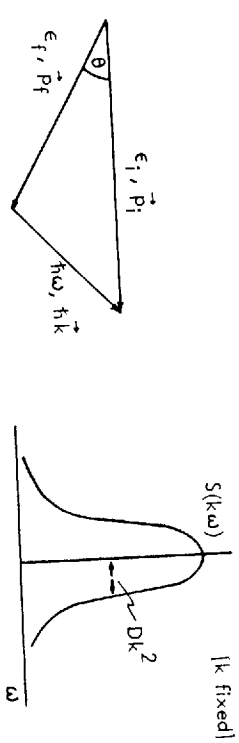


Fig. 2.2

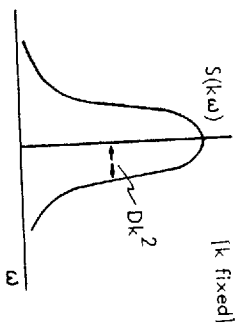


Fig. 2.3

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 Dk^2 . Thus, one can measure the spin diffusion coefficient since the [factors] do not involve the frequency shift ω . 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 ω 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 χ "? 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, χ 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^{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 χ 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. χ 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 He³ 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 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,

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

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 δh^{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 ρ^0 is in detail but it is presumed known. Since the system usually starts out from thermal equilibrium, an appropriate choice for ρ^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 ω , and that it only depends on $k = |\vec{k}|$, since χ'' 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 ω 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,

$$\delta h^{\text{ext}}(\vec{r}, t) = \int \frac{d^n k}{(2\pi)^3} e^{-i\vec{k}\cdot\vec{r} + ik^2 t} \delta h^{\text{ext}}(\vec{k}, t), \quad (2.48)$$

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 k and z where hydrodynamics is correct, we can compare (2.54) and (2.9), and obtain

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

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

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

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 $[\chi \equiv \chi(k \rightarrow 0)] \delta \epsilon \langle M(k) \rangle = \chi \delta h(k)$ 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 χ 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

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

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

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

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 $(1/\hbar\omega)(1 - e^{-\hbar\omega/kT}) \delta(\omega) = \beta \delta(\omega)$ 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 ω 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 χ'' 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 ω . 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 ω , 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." (Schriderhannes)

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)

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

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

$$\chi''_{MM}(r-r',\omega) = (1 - e^{-i\omega\beta}) S_{MM}(r-r',\omega), \tag{2.68}$$

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 $\omega\chi''(k,\omega)$

We pointed out after eq. (2.44) that

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

The significance of this property is already clear from the foregoing. From (2.56) we see that it implies that the spin magnetic susceptibility χ 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 $S(k,\omega) \geq 0$, it is necessary for the interpretation of the function $S(k,\omega)$ 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

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

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

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

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

$$S_{MM}(k,\omega) \geq 0 \text{ or } \omega\chi''_{MM}(k,\omega) \geq 0. \tag{2.73}$$

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

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

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

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

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 ω 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

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

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

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

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 $[1 - \omega/z]^{-1} = 1 + (\omega/z) + (\omega/z)^2 + \dots$ 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 ω 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 χ'' 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 τ , 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, $(\omega/Dk^2)_{\omega \ll \tau} \ll 1$,

(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, τ . However, τ 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 τ_c of eq. (2.11). Semiquantitatively, (2.86) is a very useful result.

In He³ 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 τ 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

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

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

$$\int_{-\infty}^\infty \frac{d\omega}{\pi} \chi''(k, \omega) = k^2 \int_{-\infty}^\infty \frac{d\omega'}{\pi} D'(\omega')$$

or

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

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

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

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). τ 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 ω , and a function of $|k|$ 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 , $D'(ku)$ is a simpler object than $X''(kx)$, and approximations to $D'(ku)$ 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 $\text{Im}z < 0$ but the 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

