

Since our derivation of X'' 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

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

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 $X''(k, \omega)$ 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 Nürnberger hängen keinen, sie hätten 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

$$S_{ij}(t) = \langle A_i(t) A_j(0) \rangle - \langle A_i(t) \rangle \langle A_j(0) \rangle, \quad (2.64a)$$

$$X_{ij}''(t) = \langle \frac{1}{2\hbar} [A_i(t), A_j(0)] \rangle. \quad (2.64b)$$

We have subtracted the equilibrium averages in (2.64a) so that $S_{ij}(t) \rightarrow 0$ as $t \rightarrow \infty$, 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 $\rho = e^{-\beta H} / \text{tr } e^{-\beta H}$. Because the operator, $e^{-\beta H}$, effects a time translation by the imaginary time $\tau = i\hbar\beta$, see (2.42a),

$$\begin{aligned} \text{tr } e^{-\beta H} A_i(t) A_j(0) &= \text{tr } A_i(t + i\hbar\beta) e^{-\beta H} A_j(0) \\ &= \text{tr } e^{-\beta H} A_i(0) A_j(t + i\hbar\beta), \end{aligned} \quad (2.65)$$

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

$$S_{ij}(-t) = S_{ij}(t - i\hbar\beta) = e^{-\beta \hbar \partial_t} S_{ij}(t), \quad (2.66)$$

And thus easily from (2.64)

$$2\hbar X_{ij}''(t) = S_{ij}(t) - S_{ij}(-t) = [1 - e^{-\beta \hbar \partial_t}] S_{ij}(t), \quad (2.67a)$$

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

$$2\hbar X_{ij}''(\omega) = (1 - e^{-\hbar \omega \beta}) S_{ij}(\omega). \quad (2.67b)$$

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

where

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

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,

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

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

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

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

$$\int \frac{d^3x}{\pi} \omega \chi''(k; \omega) = \frac{\hbar^2}{m} \mu^2 k^2. \quad (2.78)$$

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

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

where

$$\langle \omega^{(n)}(k) \rangle = \frac{\int \frac{d^3x}{\pi} \omega^n \chi''(k; \omega) / \omega}{\int \frac{d^3x}{\pi} \chi''(k; \omega) / \omega}. \quad (2.79b)$$

From its derivation which expands $[1 - \omega/z]^{-1} = 1 + (\omega/z) + (\omega/z)^2 + \dots$ it is clear that this expansion can only be asymptotic. It is valid when $|z|$ is "large compared to all frequencies in the system" which means, all frequencies ω for which $\chi''(k; \omega)$ is not effectively zero.

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

$$\chi''(k; t) = \frac{1}{z} \sum_{n=0}^{\infty} \frac{(-it)^n}{n!} \langle \omega^{(n+1)}(k) \rangle \chi(k), \quad (2.80)$$

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

2.10 Relaxation Time Approximation

An interesting feature of the sum rules is their very existence. There is no reason why the thermodynamic average of the multiple commutators in (2.75) should not exist, for all n , and in many cases this can in fact be rigorously proved. This means, then, that $\chi''(k; \omega)$ has to fall off sufficiently rapidly at large ω so that all of its moments are finite.

Evidently, the hydrodynamic approximation for $\chi''(k; \omega)$, eq. (2.55b), does not have this property. Indeed, while it exhausts the "thermodynamic" sum rule (2.56), it fails to satisfy even the first high-frequency sum rule (2.78). The Lorentzian dies off too slowly in the wings.

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

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 ^3He 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 $\chi''(k_{||})$ is somewhat improved from eqs. (2.55) to (2.83), all higher frequency moments $\langle \chi''(n)(k) \rangle$, $n \geq 4$, 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

$$\chi(kz) = \frac{ik^2 D(z)}{z + ik^2 D(z)} \chi, \quad (2.87a)$$

which makes it plain that what the "constitutive equation with memory" (2.81) does is introduce frequency dependence into the transport coefficient. Here

$$D(z) = \int_0^{\infty} e^{izt} D(t) dt = \int_{-\infty}^{\infty} \frac{D'(u)}{z - u} du \quad (1mz > 0), \quad (2.87b)$$

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

$$\chi''(k_{||}) = \frac{uk^2 D'(u)/2}{[v + k^2 P \int_{-\infty}^{\infty} \frac{D'(u')}{x - u'} dx]^2 + [k^2 D'(x)/2]^2} \quad (2.87c)$$

The function $D'(u)$ must therefore be positive.

From (2.87c) or more easily from (2.87d) it is easy to see that the first n moments of $\chi''(k_{||})$ will be finite if we choose a $D'(u)$ whose first n moments are finite. In particular, the f -sum rule is fulfilled if

$$\int_{-\infty}^{\infty} \frac{du}{\pi} u^f \chi''(k_{||}) = k^2 \int_{-\infty}^{\infty} \frac{du}{\pi} D'(u) \quad (2.88a)$$

or

$$D(t=0) - \int_{-\infty}^{\infty} \frac{du}{2\pi} D'(u) = \frac{\eta\mu^2}{m\chi} \quad (2.88b)$$

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 should be overly impressed by these general results. The complexity of a many-body problem does not disappear quite so easily. Since it leads to finite moments of any order, one often prefers a Gaussian memory

$$D(t) = \frac{\eta\mu^2}{m\chi} e^{-\pi(t/2\tau)^2} \quad \text{or} \quad D'(u) = \frac{\eta\mu^2}{m\chi} (2\tau) e^{-(u\tau)^2/\pi} \quad (2.89)$$

$$\frac{1}{iz} [\chi(kz) - \chi(k)] = \int \frac{d^u x}{\pi^u} \frac{\chi''(kx)}{i^u(w-z)} = 0, \quad (2.98)$$

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

$$\operatorname{Re} \int \frac{d^u w}{\pi^u} \frac{\chi''(kw)}{i^u(w-x) + y} = \int \frac{d^u w}{\pi^u} \frac{y}{(w-x)^2 + y^2} \frac{\chi''(kw)}{w} \neq 0 \text{ if } y \neq 0 \quad (2.99)$$

cannot vanish anywhere ($y \neq 0$) since $\chi''(kx)/x$ is non-negative, and thus (2.98) cannot vanish for $\operatorname{Im} z \neq 0$. 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 $\chi''(kx)$. That is not awfully much since it just introduces another unknown function $D'(kx)$ to describe $\chi''(kx)$. And indeed, many different kinds of dispersion relations can easily be proved (Kadannoff and Martin 1963). What makes the present one nonetheless valuable is that in the important region of small k and x where $\chi''(kx)$ has a complicated analytic structure, $D'(kx)$ is presumably well-behaved, with its value at $k = 0$ and $x = 0$ given by

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

the spin diffusion coefficient. Thus, for small k and w , $D'(kw)$ is a simpler object than $\chi''(kw)$, 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

$$\frac{1}{iz\beta} [\chi(kz) - \chi(k)] = C(kz) = \frac{1}{z + ik^2 D(kz)} i\beta^{-1} \chi(k), \quad (2.101)$$

does incorporate one important feature of the dynamics: the conservation law (2.3) is the origin of the factor k^2 in (2.101), and thus at $k = 0$, $C(kz)$ has a pole at $z = 0$. As k becomes finite, the pole migrates into the lower half z -plane, to a point $z = z^0(k)$ which is the solution of

$$z^0 + ik^2 D(k, z^0) = 0. \quad (2.102)$$

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

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

where

$$Z^{-1}(k) = 1 + ik^2 \frac{\partial D(kz^0)}{\partial z}. \quad (2.103)$$

Near $z^0(k)$ therefore

$$C(kz) = \frac{Z(k)}{z - z^0(k)} i\beta^{-1} \chi(k). \quad (2.104)$$

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

$$z^0(k) = ik^2 D(0, 0) \text{ and } Z(k) = 1, \quad (2.105)$$

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

3.1 Linear Dynamical Response

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 $\delta a_i^{\text{ext}}(\vec{r}, t)$, the

Hamiltonian in the presence of these fields is given by

$$\mathcal{K}(t) = H - \sum_i \int d\vec{r} A_i(\vec{r}, t) \delta a_i^{\text{ext}}(\vec{r}, t) \quad (3.1)$$

in Schrödinger representation. As in section 2.5 we calculate by time-dependent perturbation theory the linear response. That is, we want to know the induced 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 $B(\vec{r}, t)$ if we start out from equilibrium at $t = -\infty$, and let the system evolve under $\mathcal{K}(t)$.

Proceeding exactly as in section 2.5, we obtain

$$\delta \langle B(\vec{r}, t) \rangle = \sum_{i=1}^f \int_{-\infty}^t dt' \int d\vec{r}' \left\langle \frac{i}{\hbar} [B(\vec{r}, t), A_i(\vec{r}', t')] \right\rangle \delta a_i^{\text{ext}}(\vec{r}', t'). \quad (3.2)$$

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

$$\delta \langle A_i(\vec{r}, t) \rangle = \sum_{j=1}^f \int_{-\infty}^t dt' \int d\vec{r}' \delta_{ij} \left\langle \frac{i}{\hbar} [A_i(\vec{r}, t), A_j(\vec{r}', t')] \right\rangle \delta a_j^{\text{ext}}(\vec{r}', t'), \quad (3.3)$$

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

$$\chi_{ij}^{\text{ret}}(\vec{r}, \vec{r}', t) = \chi_{ij}^{\text{ret}}(\vec{r}-\vec{r}', t-t') = \left\langle \frac{1}{\hbar} [A_i(\vec{r}, t), A_j(\vec{r}', t')] \right\rangle, \quad (3.4)$$

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

$$\chi_{ij}^{\text{ret}}(\vec{k}, \omega) = \int_{-\infty}^{\infty} d(t-t') \int d(\vec{r}-\vec{r}') e^{i\omega(t-t') - i\vec{k} \cdot (\vec{r}-\vec{r}')} \chi_{ij}^{\text{ret}}(\vec{r}-\vec{r}', t-t') \quad (3.5)$$

and the matrix of response functions by

$$\chi_{ij}(\vec{k}, \omega) = \int_{-\infty}^{\infty} \frac{d\omega'}{\pi} \frac{\chi_{ij}^{\text{ret}}(\vec{k}, \omega')}{\omega - \omega'} \quad (\text{Im } \omega \neq 0), \quad (3.6)$$

then we can write (3.3) in the form

$$\delta \langle A_i \rangle(\vec{k}, \omega) = \chi_{ij}(\vec{k}, \omega) \delta a_j^{\text{ext}}(\vec{k}, \omega), \quad (3.7)$$

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"

$S_{MM}(\vec{r}, \vec{r}', t)$ 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 $e(\vec{r}, t)$, and many 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 $S_{ne}(\vec{r}, \vec{r}', t) = [\langle n(\vec{r}, t) e(\vec{r}', t') \rangle - \langle n(\vec{r}, t) \rangle \langle e(\vec{r}', t') \rangle]$.

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

4. The Normal Fluid

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

$$I_{\text{scatt.}} \begin{pmatrix} \vec{k}_i \rightarrow \vec{k}_i - \vec{k} \\ \omega_i \rightarrow \omega_i - \omega \end{pmatrix} = [\text{factors times}] S_{nn}(\vec{k}, \omega) \quad (4.3)$$

as shown in the Appendix. The bracket contains kinematical factors which are not 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 low frequencies the spectrum found looks as shown in fig. 4.2.

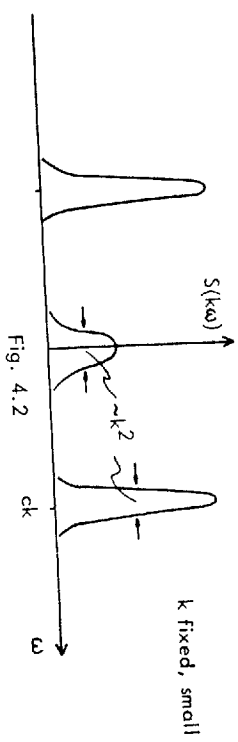


Fig. 4.2

There are three Lorentzian peaks, the central "Rayleigh peak" (caused by heat 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, just as we 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 later, our presentation, which follows the paper by Kadanoﬀ and Martin 1963, is tantamount to

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

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

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 ω_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.

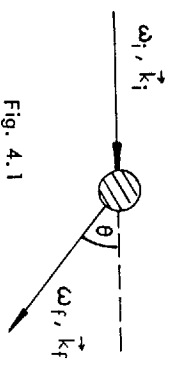


Fig. 4.1

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

shall write them all down first, and then explain.

Conservation Laws:

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

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

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

Constitutive Relations:

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

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

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

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

Thermodynamic Relations:

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

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

Here n, ϵ, p are the equilibrium values of density, energy density, and pressure, e.g., $n = \langle n(\vec{r}, t) \rangle_{\text{eq}}$. $p(\vec{r}, t), T(\vec{r}, t)$, 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 (η), bulk viscosity (ζ), and heat conductivity (κ).

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

that way; more generally, there are terms $\sim v_i v_j$ in $\langle \tau_{ij} \rangle$, for example. However, χ'' gives the linear response, and so to obtain χ'' 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 $\langle n \rangle, \langle \vec{g} \rangle, \langle \epsilon \rangle$. 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, $p(\vec{r}, t) = p_{\text{eq}}(n(\vec{r}, t), \epsilon(\vec{r}, t))$, 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 \vec{v} are given by

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

$$\tau_{ij}(\vec{r}, t) = \tau_{ij}^0 + v_i g_j^0 + v_j g_i^0 + v_i v_j m n^0, \quad (4.10b)$$

$$i_j \epsilon(\vec{r}, t) = i_j \epsilon^0 + v_i (\tau_{ij}^0 + \epsilon^0 \delta_{ij}) + v_j v_i g_j^0 + \frac{1}{2} v^2 (g_i^0 + v_j m n^0). \quad (4.10c)$$

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, $\vec{g}^0 = \vec{v}^0 = 0$, and $\tau_{ij}^0 = p^0 \delta_{ij}$. 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).

$$C_{\uparrow}(kz) = \beta^{-1} \int_{\pi}^{\pi} \frac{d\omega}{\pi} \frac{\chi_{\uparrow}''(k\omega)}{\omega(\omega-z)} = \frac{i\beta^{-1} m\pi}{z + ik^2 \eta/m\pi}, \quad (4.39)$$

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

$$\frac{1}{\omega} \chi_{\uparrow}''(k\omega) = \frac{k^2 \eta}{\omega^2 + (k^2 \eta/m\pi)^2}. \quad (4.40)$$

This function has, again, the familiar diffusion structure. Note in passing that the shear viscosity, η , must of course be positive; eq. (4.40) proves that since

$$\omega \chi_{\uparrow}''(k\omega) \geq 0.$$

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:

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

$$C_{\rho q}(kz) = \frac{i\beta^{-1} mnc \Gamma}{z + ik^2 D_T}, \quad (4.42b)$$

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

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

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

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

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

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

$$\frac{1}{\omega} \chi_{\rho q}''(k\omega) = mnc \Gamma \frac{k^2 D_T}{\omega^2 + (k^2 D_T)^2}, \quad (4.44b)$$

$$\frac{1}{\omega} \chi_{nq}''(k\omega) = T \left(\frac{\partial n}{\partial T} \right)_p \left[\frac{k^2 D_T}{\omega^2 + (k^2 D_T)^2} - \frac{(c^2 - c^2 k^2) k^2 D_T}{(\omega^2 - c^2 k^2)^2 + (\omega k^2 \Gamma)^2} \right]. \quad (4.44c)$$

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

$$\omega \chi_{nA}''(k\omega) = \frac{1}{m} k \chi_{g_z A}''(k\omega) \quad (4.45)$$

because of particle conservation.

ments produce a wealth of information.

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

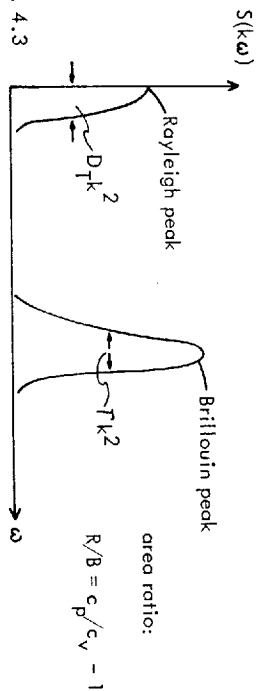


Fig. 4.3

The most immediate quantities to obtain are the speed of sound, from the position of the Brillouin line, the sound attenuation constant Γ 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 (4.27c) 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. (4.44) 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:

$$\frac{c_p}{c_v}; \left(\frac{\partial p}{\partial mn}\right)_T; D_T = \frac{\kappa}{mnc_p}; D_L = \left(\frac{4}{3}\eta + \zeta\right)/mn. \quad (4.47)$$

Quite a harvest. Note, however, what these experiments involve. The frequency shifts ω , 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

techniques, specially invented to owe the theoretician.

Suppose we could extend these measurements of $\chi''_{nn}(k; \omega)$ or $S_{nn}(k; \omega)$ to arbitrary k and ω . 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 else 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 $\int d(\omega/\pi) \omega \chi''_{nn}(k; \omega) = k^2(n/m)$. Moreover, we can obtain the static structure factor $S(k) \equiv S_{nn}(k, \omega=0)$ since

$$S(k) = k_B T \int \frac{d\omega}{\pi} \chi''_{nn}(k; \omega)/\omega, \quad (4.48)$$

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

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

$$p = n k_B T - \frac{1}{6} n^2 \int d\mathbf{r} r v'(r) g(r), \quad (4.50)$$

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

$$\begin{aligned} n^2 g(|\mathbf{r}-\mathbf{r}'|) &= \langle \sum_{\alpha \neq \beta} \delta(\mathbf{r}-\mathbf{r}_\alpha) \delta(\mathbf{r}'-\mathbf{r}_\beta) \rangle \\ &= n^2 + \int \frac{d\mathbf{k}}{(2\pi)^3} e^{i\mathbf{k}(\mathbf{r}-\mathbf{r}')} [S(k)-n], \end{aligned} \quad (4.51)$$

and $v'(r) = \frac{dv(r)}{dr}$. From e in particular, we could obtain the specific heat, $mnc_v = (\partial e/\partial T)_n$. A theoretician should therefore calculate χ''_{nn} , or better the momentum density correlation function $\chi''_{g_i g_i}$ since its transverse part $\chi''_{g_i g_i}$ determines

For the transport coefficient λ_{AB} associated with the conserved variables A, B. As it happens, the normal liquid has only diagonal λ 's. λ_{AB} would appear in constitutive relations in the form

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

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

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

$$\partial_{\vec{t}} A(\vec{r}, t) + \vec{\nabla}_{\vec{t}} \cdot \vec{A}(\vec{r}, t) = 0 \quad \text{and} \quad \partial_{\vec{t}} B(\vec{r}, t) + \vec{\nabla}_{\vec{t}} \cdot \vec{B}(\vec{r}, t) = 0. \tag{4.56}$$

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)

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

where $\vec{j}_2 = \vec{k} \cdot \vec{r}$ is the longitudinal component of the current density. (There is no need to subtract the constant terms $\langle \vec{r}^{\vec{A}} \rangle \langle \vec{r}^{\vec{B}} \rangle$ 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

$$\kappa T = \lim_{\omega \rightarrow 0} \lim_{k \rightarrow 0} \frac{1}{12k\omega T} \int_{-\infty}^{\infty} dt \int d\vec{r} e^{i\omega t - i\vec{k} \cdot \vec{r}} \langle \{ \vec{r}_2^{\vec{A}}(\vec{r}, t), \vec{r}_2^{\vec{B}}(\vec{0}, 0) \} \rangle, \tag{4.59a}$$

$$\begin{aligned} \pi(\delta_{ij} + \frac{1}{3} \frac{k_i k_j}{k^2}) + \zeta \frac{k_i k_j}{k^2} &= \lim_{\omega \rightarrow 0} \lim_{k \rightarrow 0} \frac{1}{4k\omega T} \int_{-\infty}^{\infty} dt \int d\vec{r} e^{i\omega t - i\vec{k} \cdot \vec{r}} \\ &\times \sum_{m,n} \frac{k_m k_n}{k^2} \langle \{ \tau_{im}^{\vec{A}}(\vec{r}, t), \tau_{in}^{\vec{B}}(\vec{0}, 0) \} \rangle. \end{aligned} \tag{4.59b}$$

These results make it evident that not only κ , π and $\frac{4}{3}\pi + \zeta$, but also ζ are positive. Pretty 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., \vec{T}_{ij} , $\vec{r}^{\vec{A}}$) are not, in general, themselves conserved. Consequently, fluctuations of the total current $\vec{J}^{\vec{A}}(t) = \int d\vec{r} \vec{r}^{\vec{A}}(\vec{r}, t)$ will decay within a finite, microscopic time, as explained in section 2.1. In the absence of long-ranged correlations, the correlation functions 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

$$\lambda_{AB} = \frac{1}{k_B T} \int_0^{\infty} dt \int d\vec{r} \left[\frac{1}{2} \{ \vec{r}_2^{\vec{A}}(\vec{r}, t), \vec{r}_2^{\vec{B}}(\vec{0}, 0) \} \right] - \langle \vec{r}_2^{\vec{A}} \rangle \langle \vec{r}_2^{\vec{B}} \rangle, \tag{4.60}$$

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 $\vec{r}^{\vec{A}}$ and $\vec{r}^{\vec{B}}$ are not.

Now the longitudinal momentum density $g_{\vec{t}}(\vec{r}, t)$ is the current of the conserved mass density $m(\vec{r}, t)$. However, $g_{\vec{t}}$ obeys itself a continuity equation, with the current τ_{zz} , taking $\vec{k} = k\vec{z}$. According to the argument given above, the zz-component of (4.59b) which gives $\frac{4}{3}\pi + \zeta$, should thus converge, and following the equations backwards to (4.53b) this means that for small but finite ω