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*Lectures on*  
The Many-Body Problem

Edited by  
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## Preface

The lectures collected in this volume were delivered at the Fifth International School of Physics, which was held at Ravello from April 17 to May 4, 1963, thanks to the generous support of the Advanced Study Institute Programme of NATO.

The subject chosen for this School was again the Many-Body Problem, to which part of the first and all of the second School were also dedicated. The advances made in the last years in this field have been indeed of the greatest importance, so that the present volume offers a new panorama, and deeper perspectives than the previous ones.

I gratefully acknowledge here the warm and friendly collaboration of the distinguished lecturers who made this School a rewarding experience for all, from all points of view. In particular, I feel indebted to Professor D. Pines, whose advice and help have been extremely valuable at all stages of this endeavor. Special thanks are also due to Academic Press for their understanding cooperation and assistance.

E. R. CAIANIELLO

*November, 1964*

# Introductory Remarks on Solid-State Physics

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The purpose of these introductory lectures will be to give a brief review of some of the typical situations encountered in solid-state theory and to identify those which are difficult to solve and therefore call for the techniques of many-body theory which will form the subject of the later discussions.

By far the simplest case is that of the electronic ground state of a nonconducting solid. We may picture this as an assembly of atoms, molecules, or ions with closed-shell configurations, such as a solid noble gas, or an ionic crystal like NaCl. Each separate atom or ion is in a unique quantum state (neglecting nuclear spin) separated from the next higher level by an energy gap of several electronvolts. We can therefore be sure that the electron system in the crystal is still in a single, nondegenerate quantum state, and there is still an appreciable energy gap to the next excited state. (However, the first excited electron state will, in general, form the beginning of a continuum, as we shall see.)

The wave function and energy of the electron state depend on the position of the nuclei, but they may be determined as if the nuclei were fixed, since the motion of the nuclei is slow. We are here relying on the familiar adiabatic approximation, which is valid provided the nuclear displacement  $d$ , which causes a substantial change in the electronic wave function divided by the nuclear velocity  $v$ , is large compared to the electronic period. In other words,

$$\frac{d}{v} \gg \frac{\hbar}{\Delta E}$$

where  $\Delta E$  is the lowest excitation energy.

It should be stressed that we do not claim that the electronic state of each atom can be approximately described by that of a free atom; in a realistic crystal the mutual disturbance of the atoms is substantial. We use only the fact that this disturbance is not large enough to diminish the energy gap in order of magnitude, or to invert the sequence of energy levels. It is possible that even starting from atoms with a degenerate ground state the degeneracy may be removed in the solid, so that there is a substantial energy gap, and the crystal is an insulator as, for example, in the case of diamond.

For a nonconducting crystal in the electronic ground state, we may therefore treat the nuclei as moving in a static potential, which is just the electronic energy as function of the position of the nuclei. The position is quite similar to the problem of a diatomic molecule, for which the adiabatic approximation is usually set up, except that instead of one coordinate, the internuclear distance, we are dealing with a large number of variables.

The potential energy which is thus defined reaches its lowest value for a configuration which forms a perfect lattice, and for small oscillations around this equilibrium configuration we may expand the potential energy in powers of the displacements; symbolically:

$$U = U_0 + \sum A_{n,n'} u_n u_{n'} + \dots$$

where  $u_n$  is the displacement of the  $n$ th atom, both  $n$  and  $n'$  being vectors. The linear term is absent since  $u_n \equiv 0$  is an equilibrium configuration.

The series may be expected to converge rapidly if the displacements are small compared to the interatomic spacing:  $u \ll a$ . (Strictly speaking, we require only that  $|u_n - u_m| \ll a$ , where  $n$  and  $m$  are two atoms with a substantial interaction between them, since a uniform displacement of the crystal does not affect the potential energy.) For most crystals this condition is well satisfied even near the melting point, but for some exceptional cases, notably in solid He, even the zero-point motion has an amplitude comparable with  $a$ . These cases are very hard to analyze.

Otherwise, a good approximation is obtained by neglecting all terms higher than the second in the series for  $U$ , and the result is coupled harmonic motion (which in a well-known way can be solved by the use of normal coordinates) whose quanta of oscillation lead to the concept of phonons.

In this sense even the simple case of the nonconducting crystal represents a many-body problem, but it is of a specially simple kind, since in the harmonic approximation the different normal modes (or the different phonons) are independent. The situation is similar to that of the perfect gas, which is really an assembly of one-particle problems. As in the case of the nearly perfect gas, one is forced to consider collisions even if they are small, because they produce qualitatively new effects. In the harmonic crystal, as in the perfect gas, the transport coefficients, such as the thermal conductivity, are infinite, and a realistic approach relies on anharmonic terms, which cause changes in the phonon distributions, just as collisions in the gas cause changes in the velocities of the molecules.

The exact treatment of "phonon collisions" due to anharmonic terms in the potential is rather difficult, but it represents a problem in statistical mechanics rather than a typical many-body problem. Some features of the phonon collisions can be studied very directly in experiments on neutron scattering. If the neutron wavelength is too long for Bragg scattering to occur, each scattering must involve the creation or annihilation of at least one phonon. By observing the energy and momentum change of the neutron, one therefore expects to see the energy-momentum relation for phonons. Multiphonon processes give a broad background, the one-phonon effect represents a peak which would be a sharp line in the harmonic limit. Its width is a measure of the phonon lifetime; its relation to the imaginary part of the energy of a one-phonon state, as defined by a one-phonon Green function, is an interesting subject for study.

There is apparently some indication that for this phonon decay processes in which two phonons are absorbed and two created, are as important as those in which two go into one or vice versa, although the former are due only to the quartic terms in the potential energy, or come from the operation of the cubic terms twice through a virtual intermediate stage. This may be due to the fact that the three-phonon processes can happen only in special circumstances which are rather sensitive to the energy-momentum relation for phonons, and thus represent a rather small amount of phase space.

Cubic and quartic terms are also responsible for thermal expansion. In the presence of thermal expansion one might be doubtful about the

validity of the Taylor series for the potential energy, since the distance of two atoms at opposite ends of the crystal is now  $N(a + \delta a)$  instead of  $Na$ , so that either or both must have moved an amount  $N\delta a$  from the equilibrium position. It was stressed earlier that we require only the relative displacement of interacting atoms to be small, and this will always be the case, so that there is no reason to be doubtful about the validity of the series.

However, the convergence can be improved by expanding about the equilibrium configuration at the given temperature. The fact that the meaning of the variables then depends on the temperature causes no fundamental difficulty, though it requires some care in dealing with fluctuation problems.

The next problem in increasing order of complexity is that of a semiconductor, which we can regard as an insulating crystal with a few additional electrons (or a few electrons removed). As long as the number of carriers is small, we may treat them as independent, and therefore the basic problem is that of one additional electron (or one hole). In a perfect crystal, treating the nuclei for the moment as being fixed, the translational symmetry requires that the electronic wave function changes only by a phase factor upon a displacement of the whole system by one lattice constant. Calling this factor  $\exp(ika)$ , one defines a wave number  $k$  in each direction, and thus a wave vector  $\mathbf{k}$ .

By imagining this state built up adiabatically from separated atoms, or from noninteracting electrons we are led to expect that the lowest energy for any given  $\mathbf{k}$  will be discrete, so that there exists a function  $E(\mathbf{k})$ , as in the case of a single electron moving in a periodic potential.

In reality, this is not the energy of a single electron, but a state of a many-electron system, since the last electron interacts with all the electrons in the closed-shell atoms. In the language of many-body theory  $E(\mathbf{k})$  is the energy of a "quasi-particle." However, it would be pedantic to insist on this usage. Indeed in the physics of elementary particles we invariably deal with particles which interact strongly with fields in which they are embedded, and if we were pedantic we should always talk about quasi-protons, quasi-mesons, etc.

If we start from an insulator with a small energy gap, thermal excitation will produce electron-hole pairs ("intrinsic" semiconductor) the electron and the hole may separate and can then be treated as inde-

pendent. They may, however, also remain bound to each other by their coulomb interaction. This is called an "exciton." The motion of the exciton as a whole is again characterized by a single wave vector  $\mathbf{k}$ , with the energy being a function of  $\mathbf{k}$ . However, there are also internal degrees of freedom. For a state in which the mean distance of the electron and the hole is large compared to the lattice spacing  $a$ , these can be described by a continuum theory, resembling the theory of positronium, except that the effective mass of electron and hole, and the dielectric constant of the crystal, alter the scale factors. There is some doubt, however, whether this description is applicable to the low-lying levels of the system, in which there is an appreciable probability of the electron and hole being in the same atom, so that the atomic structure of the crystal is clearly vital.

Another type of exciton may be pictured as an excitation of an atom in the crystal without an appreciable probability of an electron leaving the atom. A typical example of this is provided by the optical excitation of rare-earth atoms in crystals, in which the excitation is in one of the inner, shielded shells so that it is affected only slightly by the neighboring atoms. In this type of exciton one also finds a continuous energy spectrum, characterized by a single function  $E(\mathbf{k})$  of a wave vector, which determines the propagation of the excitation through the crystal.

Dr. Pines has pointed out in this discussion the existence of a plasmon mode also in an insulating crystal. This can be visualized as a collective state made up of a coherent superposition of all possible particle-hole pairs, including not only all possible relative momenta of particle and hole, but also all possible particle and hole bands. The energy of this mode lies fairly high and its description requires more specific model assumptions or approximations than the low-lying states enumerated above, whose nature follows directly from conservation laws, together with considerations of adiabatic changes from simpler systems.

In a real crystal all these modes are coupled with the lattice vibrations, so that there is an electron-phonon, hole-phonon, exciton-phonon, or plasmon-phonon interaction. This alters (renormalizes) the energy of the excited mode and also leads to real scattering and thus to a finite lifetime and finite transport coefficients for these modes.

An especially interesting example is the additional electron in a polar

crystal. Because of the long range of electric interactions, the coupling with optical phonons is here particularly strong, and also particularly simple since its major part can be treated in a continuum approximation. Since a substantial lattice distortion accompanies the moving electron the renormalization of its inertial mass may be appreciable.

The situation becomes more complex when we consider a metal, for two reasons: (a) The definition of the effective forces between the nuclei, and hence of the lattice vibrations does not apply any more, (b) the electronic excitation spectrum not only has no threshold, but has many states with the same wave vector.

As regards the first point we notice that the usual justification of the adiabatic approximation, which we have used to define the lattice potential for the insulating crystal, clearly fails when there is a continuous spectrum, since the condition for its validity contains the energy gap. Even if one tried hopefully to ignore this condition and to calculate the energy of the electron system as a function of the nuclear coordinates it would be hard to make this unique since it is then not clear what is meant by specifying a given electronic state for different such configurations. (This could be done if one restricted oneself always to the lowest electronic state, but in the continuum this would be quite unrealistic.) One way of overcoming this difficulty is to start with the effect of electrons in closed shells only, and replacing the conduction electrons by a uniform static charge distribution, to avoid unphysical space charge effects. This part of the problem is like that of an insulating crystal. The answer it gives for the lattice vibrations is unrealistic, since it does not allow properly for the effects due to the conduction electrons, in particular for the screening of longitudinal vibrations, and this has then to be corrected; the corrections appear formally as electron-phonon interactions, but treated in this way they are appreciable and have to be handled better than low-order perturbation theory.

On the second difficulty it is evident that for a system of noninteracting electrons in a static potential there are many excited states of the same momentum  $q$ . If  $\varepsilon(p)$  is the energy of one electron, transfer of one electron gives an energy change,  $\varepsilon(p + q) - \varepsilon(p)$ ,  $p$  being an occupied state and  $p + q$  empty which is least for  $p$  and  $q$  parallel and  $p + q$  just outside the Fermi surface. From this minimum the excitation spectrum extends upward. Lower states of the same momentum can be produced by excit-

ing more particles. The absolute minimum is obtained by sharing the momentum equally by all particles, when the energy increase is negligibly small.

A powerful approach to the problem, due to Landau, is to consider a state with one electron added to the system. For noninteracting electrons this will have a definite energy  $\varepsilon(q)$  if all the other electrons remain in their previous states. In the presence of interactions this is no longer a definite stationary state, but it is plausible that there should be a long-lived state with an energy which is a definite function of momentum, and with a finite life time, i.e., a finite width. For very low excitation energy (i.e., electrons close to the Fermi surface) the width is small compared to the energy and therefore the concept of such one-particle states (or quasi-particles) is useful. For very high excitations it is still possible to define a decaying state, but its properties then become dependent on the precise details of its definition.

Similarly one can define a quasi-hole by considering the states formed by removing one electron from the system. The excitations of the system can then be built up by putting in an equal number of particles and holes. As long as that number is small, the states can be described as those of single quasi-particles and holes, with interactions between them. At the same time one must of course include the interactions with phonons. That these complications are not academic is made evident by the existence of superconductivity. The possibility of this arises from the fact that the large number of coupled degrees of freedom opens up the possibility of strong correlations which make the dynamics of the system quite different from the uncoupled one.

It is normal to ignore most of these complications in the nonsuperconducting metals and even in the normal state of a superconductor above the transition point. There is indeed no experimental evidence that anything special happens in a superconductor slightly above the transition temperature (as opposed to the case of a ferromagnet above the Curie point) and this point of view may well be justified.

In that case one obtains the usual description in terms of electrons, phonons, and their collisions, in which the energy of each is again assumed to contain all the interactions, except those that give rise to real collisions.

Even in this simple framework there are nontrivial questions. One

of them concerns the matrix element of the electron-phonon interaction, which is usually written in first-order perturbation theory, based on a Taylor expansion of the potential energy of an electron in terms of the nuclear displacements. Since, however, the potential in the interior of an atom is very strong, this is hardly justified, and a much better approach is to treat this interaction in terms of a "pseudopotential" which is designed to give the correct scattering by one atom when treated in first-order Born approximation. Since the definition of a pseudo-potential depends on the medium in which the scattering takes place, the use of such a concept in the case of a solid requires considerable care.

Among the challenging simple problems is that of an electron system without a lattice, containing only a uniform positive charge distribution for neutralization. This is a problem with a single parameter, namely, the density. At high densities the electrons are not very strongly correlated and a perturbation treatment is relatively easy. F. Bloch conjectured many years ago that for low density this system would become ferromagnetic. If all electron spins are made parallel this increases the kinetic energy, since the Pauli principle then requires a Fermi surface of greater volume, but the mutual electrostatic interaction is reduced since the antisymmetrization of the orbital wave function keeps the electrons apart in space. Low density favors the second factors as compared with this first, but a quantitative treatment of this problem is difficult. The simple perturbation theory used by Bloch is certainly invalid when it predicts ferromagnetism. At very low density the electrons almost certainly form a lattice, and in the extreme case, in which the zero-point amplitude is much less than the spacing, there is no opportunity for ferromagnetism. Its occurrence at somewhat higher densities is not settled but seems unlikely.

Another interesting problem in solid-state theory is that of ferromagnetism. Here it is usual to idealize the situation by assuming that the number of electrons in each atom is fixed. This appears to contradict the picture of conduction electrons in metals which we have used so far, but one must remember that magnetic electrons in the ferromagnetic metals always are inner  $d$ -electrons which belong to a narrow band, and therefore their tendency to run about independently of each other is probably not too strong. Another complication usually disregarded is the fact that  $d$ -electrons have orbital moments. For free atoms the

orientation of the orbital angular momenta would represent important degrees of freedom. In the crystal these are in some way locked to each other so that they are in a definite nondegenerate state, but the resultant anisotropy of each atom should complicate the problem of the interaction of the spins.

Apart from these complications one is then dealing with a problem in which the total number of states for the whole crystal is  $N^{(2S+1)}$  where  $S$  is the spin of one atom, this is a large, but finite number, and the spectrum of magnetic energies covers a finite energy interval. The structure of this energy spectrum is again a typical many-body problem.

Its Hamiltonian is usually obtained from the Heitler-London approximation, although recently some doubt has arisen about justification of the Heitler-London procedure for finding the relation position of different spin states.

## **Discontinuities in the Drift Velocity of Ions in Liquid Helium**

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The purpose of this short paper is to call attention to some experiments recently carried out by our group (1, 2). First, we shall briefly recall their relevant experimental features, and then we shall propose a tentative explanation which should be substantiated by a proper theoretical treatment.

We have investigated the behavior of the drift velocity  $V_d$  of electric elementary charges (here called simply "ions") (3) in liquid helium at about 1°K as a function of the applied electric field  $E$ . Two experimental method were employed using two quite different techniques, and they gave quite consistent results. In the first method the time of flight of the ions between fixed electrodes was measured in different experimental conditions by AC electronics, while in the second one the drag suffered by an ionic beam in the normal fluid current was measured (heat-flush method).

In summary, the main results were as follows.

(a) The drift velocity of ions moving in liquid helium no longer increases linearly with the increasing field but suffers a sharp discontinuity. While the value of this critical field  $E_c$  depends on the temperature, the corresponding critical velocity  $V_c$  is a temperature-independent quantity.

(b) Increasing the applied field, other discontinuities of the drift velocity are found at values which are larger integers of the first one, indicating a periodical multiplicity of the phenomenon.

(c) The first discontinuity for positive ions is found at  $V_c = 5.2 \pm 0.2$  meters/sec in a temperature range where the mobility  $\mu = V_d/E$  changes

by a factor of 3. The relative change of the mobility at the discontinuity  $\Delta\mu/\mu$ , ranges from 5 to 10%.

(d) The negative ions also show discontinuities at drift velocities which are multiples of 3.5 meters/sec. It is more difficult to observe sharp transitions for this kind of ions.

(e) Bath disturbances induced by vibrations and temperature fluctuations cause these discontinuities to disappear. What at one time was thought to be a kind of hysteresis which could sometimes prevent the transition at  $V_c$ , is now believed to be the effect of uncontrolled bath disturbances.

(f) The value of  $V_c$  is not affected by a change of a factor 20 in the ionic density of the beam and by big changes of its geometry, and within the experimental error is the same in both the experimental methods.

(g) A proper analysis of the heat-flush process indicates that the new interaction, which set in at  $V_c$ , is due to the normal fluid and not to the superfluid component.

So far the experimental results. We believe that from (f) one can derive the conclusion that this phenomenon is not due to a cooperative effect in the ionic beam, but to a process which involves only single ions. The numerical value of  $V_c$  rules out the direct production of rotons or phonons by the well known Landau criterion. The sharpness of the transition indicates that the process involves a time scale large in comparison with the ion-roton collision time, which is responsible for the mobility value before the first discontinuity. Therefore, we must look for a process in which a single ion can suffer periodical increases of interaction with the normal fluid.

We will now put forward a tentative explanation which requires concepts already familiar in the actual picture of liquid helium. We think the essential feature of the strange behavior of the ions to be due to the formation of a quantized vortex ring in the superfluid, at a value of the drift velocity consistent with the Landau criterion, and that this vortex ring remains closely bound to the ion in motion while interacting with the roton sea, so giving rise to a new source of dissipation. This picture will be qualitatively discussed in the following paragraphs.

The occurrence of quantized vortex rings in superfluid helium has

been predicted by Onsager (4) and Feynman (5), and the energy and momentum expressions suggested by Feynman are such to allow a critical velocity of the order of magnitude observed by us if the radius of the ring is about  $10^{-6}$  cm, which is the expected size if the ring must be close to the complex entity which we simply called the "ion." From the multiplicity of the quantized circulation the periodicity in the discontinuity of the drift velocity follows at once. However, the Feynman expressions are valid for free vortices and may not be for vortical rings close to a wall. The motion of a classical vortex ring close to a sphere at rest was investigated by Lewis (6) long ago. He found a range of stability, and we hope this holds true also for a sphere in motion, provided a convenient change in the radius of the ring is made. To approximate the ions as a sphere should not change the main result, owing to the small polarizability of the helium atoms.

The interaction of a vortex line with the roton sea is suggested by Hall and Vinen (7) to be responsible for the Gorter and Mellink force, the mutual-friction force which acts between the normal and the superfluid component above the critical velocity. If one uses the Lifshitz and Pitaevskii (8) expressions for this force acting on a filament of  $10^{-6}$  cm length, one can get an interaction of the order of magnitude observed in the mobility change at the discontinuity. It is also realized that the higher circulation quantum numbers give rise to correspondingly higher dissipations. This multiplicity is not observed in capillaries or slits probably because in these cases the vortex filaments or the large rings are not stable and they soon generate a tangled mass of vortical lines, generally described as superfluid turbulence. The ion instead, owing to its spherical geometry and to its small dimensions, can permit a stable quantum vortex to live safely for a long period and in different quantum numbers.

The creation of a vortex ring close to the ion is a process still obscure to us, but it is certainly not more obscure than the creation of a large vortex ring in a capillary; also in this case a long relaxation time must be assumed (9). Notice that a backflow of superfluid must always exist around an ion in motion, and this flow has the same dipolar character as the one generated by a small vortex ring placed in the center of the sphere. This fact may help in the building-up process.

In conclusion the picture suggested here uses the same kind of argu-

ments as the ones used currently to provide a possible explanation for the critical velocities observed in capillaries or slits. These arguments are not too firmly grounded to theory (10). For instance, our picture suffers from the lack of proper theoretical treatment of the behavior of a small quantum vortex ring close to a sphere. What is the creation process, what are the correct energy and momentum expressions for the ring, what are its stability conditions? These questions are left to theoreticians. We point out the interest of these questions in order to prove the correctness of our picture and therefore of the multiplicity of the quantized circulation, which plays an essential role in it. So far this multiplicity has not been proved experimentally, the Vinen (11) vibrating wire experiment being indicative of the existence of the first quantum of circulation only; this experiment is not yet generally accepted theoretically (10).

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# **Density Fluctuation Excitations in Many-Particle Systems**

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## **I. Density Fluctuation Excitations: Collective Modes in Fermion Systems**

### **A. INTRODUCTORY CONSIDERATIONS**

The quasi-particle spectrum of a many-body system is not easily measured. Its direct measurement requires that one have a source of particles, since the quasi-particle properties derive from the behavior of the system with one additional particle [or hole]. Thus while in principle one can learn about quasi-particle spectra in metals through a positron annihilation experiment [one thereby creates a hole in the electron system], in general, experiments which create or destroy a single particle in an energy range of interest are not easily devised. The usual measurement of microscopic system properties by means of an external probe involves rather the scattering of a quasi particle from one state to another or what is equivalent, the creation of a quasi-particle, quasi-hole pair.

The present lectures are intended as an introduction to the study of such pair excitations. As a prototype, we consider that class of pair excitations which correspond to a density fluctuation of the system particles. The elementary excitations associated with the density fluctuations may be measured by means of an inelastic particle-scattering experiment. We describe such an experiment, and show that what is measured corresponds to a spectral density for the density fluctuation excitation

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spectrum; that spectral density is known as the dynamic form factor. The elementary excitations which contribute to the dynamic form factor are shown to be of two kinds. The first consist of configurations which involve a single quasi-particle, quasi-hole pair, two quasi-particle, quasi-hole pairs, etc., all of which add incoherently. The second, a collective mode of the system, represent a coherent, correlated motion of a large number of system particles.

In this first lecture we shall consider the dynamic form factor for fermion systems. Following a somewhat general discussion of the pair excitations, the random phase approximation is used to describe briefly the collective modes of three systems: quantum plasmas, classical plasmas, and neutral fermions.

In the second part of these lectures we consider, from a somewhat formal point of view, the overall system response to an external probe which is coupled to the density fluctuations of the system particles. Where that coupling is weak, the system response may be characterized by a certain generalized susceptibility, the density-density response function. For a system in its ground state, the dynamic form factor serves as the spectral density for that response function. In the limit of long wavelengths, this relation enables one to derive a sum rule for the dynamic form factor, one which involves the compressibility of the many-particle system. There is, in addition, an "*f*-sum rule" for the dynamic form factors which is valid for arbitrary wavelengths. Such sum rules are important in determining the consistency of a given theory. In addition, in the case of certain superfluid systems, the sum rules enable one to write down the exact form of the dynamic form factor in the limiting case of very long wavelengths. The systems in question are liquid He<sup>4</sup> (or any system of interacting bosons) and a neutral fermion system with "s" state attractive interactions. For these systems, application of the sum rules shows that the dominant long-wavelength density fluctuations are phonons, with a speed of sound which is equal to the macroscopic sound velocity.

The above concepts are first developed for a system in its ground state. The generalization to finite temperatures is straightforward. The principal difference is that the spectral density which measures the system response is no longer equal to the dynamic form factor. The latter offers a measure of the fluctuations in the system density. In thermal equi-

librium the two spectral densities are simply related; the relation is the well-known fluctuation-dissipation theorem.

In the third part of the lectures we discuss the dielectric response functions for homogeneous electron systems. We shall derive the following exact relation between the long-wavelength static dielectric constant and the macroscopic isothermal sound velocity:

$$\lim_{q \rightarrow 0} \epsilon(q, 0) = 1 + \frac{\omega_p^2}{s^2 q^2}.$$

Here  $\omega_p^2$  is the electron plasma frequency,  $s$  the isothermal sound velocity. This relation serves to specify the screening action of the electrons for both quantum and classical plasmas, and, as well, for superconductors, in the long-wavelength limit. Moreover, application of the sum rules for the spectral density of the density-density response function shows that in this limit plasma oscillations at frequency  $\omega_p$  represent a well-defined excitation mode for *any* spatially homogeneous electron system, be it a classical plasma, a quantum plasma at arbitrary temperature and density, or a superconductor.

The reader should be warned that the level of the three parts of the lectures shifts abruptly between the first and second part. Those lectures dealing with correlation and response for neutral and charged particle systems involve much more in the way of formal relationships, and less in the way of physical discussion, than the first group concerning the density fluctuation excitation spectrum. Nonetheless it seems useful to go into the formal relationships in some detail, in view of the utility of the results one thereby obtains for the limiting behavior of the dynamic form factor.

### B. INELASTIC PARTICLE SCATTERING

As a typical microscopic probe of system behavior, we consider the measurement of the energy and angular distribution of a beam of inelastically scattered particles. Examples of such probes are the scattering of fast electrons in solids or of slow neutrons in liquid helium or solids. We assume that initially the many-particle system is in its ground state with momentum zero and energy,  $E_0$ , while the particle under study possesses a momentum  $P_e$ , energy  $E_e = P_e^2/2M_e$ . Let  $P_e - q$  be the mo-

momentum of the particle after the scattering act; by conservation of momentum and energy the system (which we take to be translationally invariant) will then possess a momentum  $q$  and an energy

$$E_n = E_0 + \frac{\mathbf{q} \cdot \mathbf{P}_e}{M_e} - \frac{q^2}{2M_e}. \quad (1.1)$$

It is convenient to characterize the scattering act by the momentum transfer  $q$  and an energy transfer  $\omega$  to the system; from (1.1), we have then

$$\omega = E_n - E_0 = \frac{\mathbf{q} \cdot \mathbf{P}_e}{M_e} - \frac{q^2}{2M_e}. \quad (1.2)$$

One sees directly that a measurement of the scattering angle  $\theta$  and the final energy of the scattered particle is equivalent to a measurement of the momentum and energy transferred to the system.

The coupling between the probe and the system may be described by a potential energy term

$$H_e = \sum_i \mathcal{V}(\mathbf{r}_i - \mathbf{R}_e) \quad (1.3)$$

where  $\mathbf{r}_i$  and  $\mathbf{R}_e$  are the system particle and probe positions, respectively. For the further analysis of the experiment, it is convenient to Fourier-analyze (1.3) as follows:

$$\begin{aligned} H_e &= \sum_i \mathcal{V}(r_i - R_e) = \sum_q \mathcal{V}_q \exp[i\mathbf{q} \cdot (\mathbf{r}_i - \mathbf{R}_e)] \\ &= \sum_q \mathcal{V}_q \varrho_q^+ \exp(i\mathbf{q} \cdot \mathbf{R}_e). \end{aligned} \quad (1.4)$$

In (1.4),  $\mathcal{V}_q$  is the Fourier transform of  $\mathcal{V}(r)$ , while  $\varrho_q$  is the Fourier transform of the particle density:

$$\varrho(r) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i) = \sum_q \varrho_q \exp(i\mathbf{q} \cdot \mathbf{r}) = \sum_i \exp[i\mathbf{q} \cdot (\mathbf{r} - \mathbf{r}_i)]. \quad (1.5)$$

In (1.5), we have assumed that we deal with a system of point particles, for which  $\varrho_q$  is given by

$$\varrho_q = \sum_i \exp(-i\mathbf{q} \cdot \mathbf{r}_i). \quad (1.6)$$

The  $\varrho_q$  describe the fluctuations in the system density about its average value

$$\varrho_0 = N.$$

(Note that because we are working with a system of unit volume, there is no distinction between the particle density,  $n$ , and the total number of particles,  $N$ .)

We assume that the Born approximation describes the scattering act. The probability for particle scattering is then proportional to the square of the matrix element of (1.4) taken between the appropriate unperturbed states of the system and the external particle. We thus see that when the probe particle makes a transition from a plane-wave state  $\mathbf{P}_e$  to another state  $\mathbf{P}_e - \mathbf{q}$ , it does so via a direct coupling to the density fluctuation  $\varrho_q^+$  of the many-body system.

The matrix element for the scattering act is

$$\mathcal{V}_q \langle n | \varrho_q^+ | 0 \rangle = \mathcal{V}_q (\varrho_q^+)_n{}_0 \quad (1.7)$$

where the state  $| n \rangle$  is an exact many-particle state of momentum  $q$ , energy  $E_n$ , which is coupled to the ground state (with wave function  $| 0 \rangle$ , energy  $E_0$ ) by the density fluctuation  $\varrho_q^+$ . According to the “golden rule” of second-order perturbation theory the probability per unit time,  $\mathcal{P}(q\omega)$ , that the particle transfer momentum  $q$ , energy  $\omega$ , to the system is given by

$$\mathcal{P}(q\omega) = 2\pi \mathcal{V}_q^2 \sum_n | (\varrho_q^+)_n{}_0 |^2 \delta(\omega - \omega_{n0}). \quad (1.8)$$

In (1.8),  $\omega_{n0} = E_n - E_0$ , the  $\delta$ -function expresses the conservation of energy (1.2), and the summation is over all states  $| n \rangle$  coupled to the ground state  $| 0 \rangle$  by the density fluctuation  $\varrho_q^+$ .

The properties of the many-particle system are embodied in the dynamic form factor

$$S(q\omega) = \sum_n | (\varrho_q^+)_n{}_0 |^2 \delta(\omega - \omega_{n0}) \quad (1.9)$$

which depends only on the system properties in the absence of the probe.  $S(q\omega)$  represents the maximum information one can obtain about the

system behavior in a particle-scattering experiment. It furnishes a direct measure of the excitation spectrum of the density fluctuations, being proportional to the squared matrix element for each permissible excitation energy. Note that  $S(q\omega)$  is real, and that it vanishes for  $\omega < 0$ , since at  $T = 0$  all the excitation frequencies,  $\omega_{n0}$ , must necessarily be positive.

### C. DYNAMIC FORM FACTOR FOR A FERMION SYSTEM

#### 1. Noninteracting Fermions

Let us consider a fermion system for which we may write

$$\varrho_q^+ = \sum_p c_{p+q}^+ c_p \quad (1.10)$$

in the representation of second quantization. The density fluctuation is thus seen to be a superposition of electron-hole creation operators of net momentum  $\mathbf{q}$ . Suppose we neglect the interaction between the fermions; the ground state wavefunction,  $\varphi_0$ , then corresponds to a filled Fermi sphere, of radius  $p_F$  in which all the particle states,  $p$ , are doubly occupied. Acting on  $\varphi_0$ ,  $\varrho_q^+$  gives rise to transitions in which a particle is destroyed in some momentum state  $\mathbf{p}$ , created in another state  $\mathbf{p} + \mathbf{q}$ . Because of the Pauli principle, the state  $\mathbf{p}$  must lie within the Fermi sphere, while the state  $\mathbf{p} + \mathbf{q}$  lies outside it. The energy of the particle-hole pair is

$$\omega_0(p, q) = \frac{(\mathbf{p} + \mathbf{q})^2}{2m} - \frac{p^2}{2m} = \frac{\mathbf{p} \cdot \mathbf{q}}{m} + \frac{q^2}{2m}. \quad (1.11)$$

We may label the states  $|n\rangle$  which enter in (1.9) by the momentum  $\mathbf{p}$  of the hole; the summation over  $|n\rangle$  becomes a sum over states  $p$  such that

$$\begin{aligned} p &\leq p_F \\ |\mathbf{p} + \mathbf{q}| &\geq p_F. \end{aligned} \quad (1.12)$$

We find therefore

$$S_0(q, \omega) = \sum_{p\sigma} n_{p\sigma}^0 (1 - n_{p+q\sigma}^0) \delta[\omega - \omega_0(q, p)] \quad (1.13)$$

where  $n_{p\sigma}^0$  is the unperturbed zero-temperature single-particle distribution function, defined by

$$\begin{aligned} n_{p\sigma}^0 &= 1, & p \leq p_F \\ n_{p\sigma}^0 &= 0, & p \geq p_F. \end{aligned} \quad (1.14)$$

Without any detailed calculation, it is clear from (1.11) and (1.13) that the excitation spectrum of particle-hole pairs will form a continuum which lies between the following limits:

$$\begin{aligned} 0 \leq \omega_0(q, p) &\leq \frac{qp_F}{m} + \frac{q^2}{2m} \quad (q \leq 2p_F) \\ -\frac{qp_F}{m} + \frac{q^2}{2m} &\leq \omega_0(q, p) \leq \frac{qp_F}{m} + \frac{q^2}{2m} \quad (q > 2p_F). \end{aligned} \quad (1.15)$$

The calculation of  $S_0(q, \omega)$  is straightforward, but somewhat lengthy because of the Pauli principle restrictions. The corresponding limit on the number of states within the Fermi sphere which contribute to (1.13) may be seen to be strongest for small values of  $q$ ; it is nonexistent for  $q \geq 2q_F$ . One finds

$$S_0(q, \omega) = \begin{cases} N(0)(\omega/qv_F) & \text{if } 0 < \omega < qv_F - \frac{q^2}{2m} \\ N(0) \frac{p_F}{2q} \left\{ 1 - \left( \frac{\omega}{qv_F} - \frac{q}{2p_F} \right)^2 \right\} & \text{if } qv_F - \frac{q^2}{2m} \leq \omega \leq qv_F + \frac{q^2}{2m} \\ 0 & \text{if } qv_F + \frac{q^2}{2m} \leq \omega \end{cases} \quad (1.16)$$

where  $N(0)$  is the density of states per unit energy at the Fermi surface for particles of one kind of spin

$$N(0) = \frac{3N}{4\varepsilon_F^0} \quad (1.17)$$

and  $v_F$  is the free-particle Fermi velocity,  $p_F/m$ .

## 2. Interacting Fermion Systems

Let us next consider  $S(q, \omega)$  for an interacting fermion system. The excited states  $|n\rangle$  which enter in the definition (1.9) of  $S(q, \omega)$  will now involve configurations of quasi particles and quasi holes. On the other hand, the expansion (1.10) of the density fluctuation  $\varrho_q^+$  refers to the simultaneous creation of a bare particle-hole pair. We are thus led to decompose a bare particle state as a sum of configurations containing one quasi particle, or two quasi particles and one quasi hole, etc. As a consequence, the density fluctuation  $\varrho_q^+$  will couple the ground state  $|0\rangle$  to excited eigenstates containing an arbitrary number of quasi-particle, quasi-hole pairs (in contrast to the noninteracting system, for which  $\varrho_q^+$  excited only a single pair of excitations). In order to maintain momentum conservation, the excited state  $|n\rangle$  must have a total momentum equal to  $\mathbf{q}$ .

The simplest such excited configuration consists in a single pair, involving a quasi hole with momentum  $\mathbf{p} \leq p_F$ , a quasi particle with momentum  $(\mathbf{p} + \mathbf{q}) \geq p_F$ . The amount of "phase space" available for such a pair is the same as for the noninteracting system. The corresponding contribution to  $S(q, \omega)$  may be written as

$$S^{(1)}(q, \omega) = \sum_{\substack{p > p_F \\ |\mathbf{p} + \mathbf{q}| < p_F}} |(\varrho_q^+)_n|^2 \delta(\omega - \varepsilon_{p+q} + \varepsilon_p) \quad (1.18)$$

where  $\varepsilon_p$  is the quasi-particle energy. In contrast to the noninteracting system, the matrix element  $(\varrho_q^+)_n^2$  is unknown, and will generally depend on  $q$  and  $\omega$ : this precludes an explicit calculation of  $S^{(1)}$ . For small  $q$ , however, the behavior of  $S^{(1)}(q, \omega)$  will resemble that for the non-interacting system: in this limit, the structure of  $S^{(1)}(q, \omega)$  is essentially a consequence of the Pauli principle, and hence is unaffected by the interaction. Thus one expects  $S^{(1)}$  to extend over a range of energies from 0 to  $q\nu_F$ , corresponding to the possible quasi-particle energies. Moreover, for small  $\omega$ ,  $S^{(1)}$  should be proportional to  $\omega$ . To see this, remark that both the quasi particle and quasi hole must lie within a range  $\omega$  of the Fermi surface. Hence the density of single-pair configurations per unit energy varies as  $\omega$ , and  $S^{(1)}(q, \omega)$  displays a comparable variation. As  $\omega$  increases, that linear variation is not, in general, followed, since

the frequency dependence of  $|(\varrho_q^+)_n|^2$  will play a role even in the long-wavelength limit.

In addition to  $S^{(1)}$ , we expect to find additional contributions to  $S$ , which arise from the coupling of the ground state  $|0\rangle$  to configurations of  $n$  quasi particles and  $n$  quasi holes ( $n > 1$ ). Since momentum conservation involves only the total momentum, there is essentially no limitation on the momentum of any single component (quasi particle or quasi hole) of these higher order configurations. As a result the excitation energy of the ( $n > 1$ ) pair configurations may be expected to vary over a broad range of the order of the Fermi energy  $\varepsilon_F$ . The corresponding contribution to  $S$  will in general, form a broad background, extending over a range of frequencies comparable to the energies of the quasi particles involved.

There are two limiting cases in which these higher pair configurations do not contribute appreciably to  $S(q, \omega)$ . The first is that of  $q$  arbitrary but  $\omega$  small; that is,  $\omega \ll \varepsilon_F$ . In this case, each of the excitations present in a given state  $n$  must lie within an energy  $\omega$  of the Fermi surface. The density of configurations of  $2n$  excitations per unit energy, each of energy  $\omega$ , varies as  $\omega^{2n-1}$ ; the contribution of the excitations to  $S(q, \omega)$  varies in the same way. As a result, the multipair configurations may be neglected in a calculation of  $S(q, \omega)$  at low, macroscopic frequencies.

The second case is that of  $q$  small ( $q \ll p_F$ ) but  $\omega$  arbitrary. Let us consider the limiting value of  $(\varrho_q^+)_n$  as  $q \rightarrow 0$ . In this limit the multipair state  $|n\rangle$  represents a well-defined excited state of the system (containing at least two quasi particles and quasi holes) which must be orthogonal to the ground state in the limit  $q = 0$  (since  $\varrho_0 = N$  and the number of particles is a constant of the motion). We conclude that  $(\varrho_q^+)_n$  is at least of order  $q$ , so that the multipair configurations give a contribution to  $S(q, \omega)$  which is at least of order  $q^2$  in the long wavelength limit.<sup>2</sup> We shall see later that the multipair configuration contribution is actually of order  $q^4$  for a translationally invariant system. It should

<sup>2</sup> This argument does not apply to the contribution to  $(\varrho_q^+)_n$  from the single-pair configurations. In the limit  $q = 0$ , an excited state with a single quasi particle and quasi hole reduces simply to a ground-state configuration. Thus for the single-pair configurations one finds  $(\varrho_q^+)_n = 1$  for the states which contribute; the number of such states is, however, of order  $q$ , so that the corresponding contribution to  $S$  extends only over a range  $q \cdot v_F$ .

be kept in mind that the argument presented here is a qualitative one (even though correct) since the quasi particles are actually well defined only in the immediate vicinity of the Fermi surface.

The modification of the pair excitation spectrum is not the only consequence of taking particle interaction into account. One finds, in addition, the possibility of collective modes of the system. A collective mode involves the correlated motion of a large number of particles. It may be thought of as an excited state in which one has a coherent superposition of all particle-hole pairs of momentum  $\mathbf{q}$ , in such a way as to produce a single excitation of energy,  $\omega_q$ , and a corresponding peak in the spectral density,  $S(q, \omega)$  in the vicinity of  $\omega_q$ . This behavior is to be contrasted with the continuum contribution arising from the incoherent superposition of particle-hole pairs, considered thus far. In general, although the collective mode is a single excitation, as compared to the substantial number (of order  $N$ ) of pair excitations which contribute to the continuous part of  $S(q, \omega)$ , it makes nonetheless an appreciable contribution to  $S(q, \omega)$ , through the coherence of the pairs which take part (again, a number of order  $N$ ). In general, the collective peaks of the spectrum are immersed in the continuum of multipair excitations. The peaks are consequently broadened, the width of the peak being related to the probability for decay of the collective mode.

When the peak falls in the range of the single-pair spectrum [i.e., of  $S^{(1)}$ ] the broadening is usually quite substantial. The peak is then best viewed as a resonance arising from the coherent motion of excited pairs. If, however, the peak lies outside the range of  $S^{(1)}$ , the broadening is comparatively small; that is,  $(\Gamma_q/\omega_q) \ll 1$  where  $\Gamma_q$  is the width of the peak. The "resonance" then becomes sharp, and it is physically more natural to consider the peak as a separate excitation of the system.

The way in which collective modes come about is best appreciated with the aid of some simple examples. The simplest approximation in which collective modes made their appearance is the random phase approximation (1, 2), in which a selected part of the interaction between the system particles is taken into account. Within the RPA (as we shall hereafter call the random phase approximation) for an electron gas, the long-wavelength collective mode is a plasma oscillation; for a system of neutral particles, it corresponds to zero sound (3). We consider next

the derivation of the density fluctuation spectrum in the RPA, and then go on to discuss the above specific examples.

#### D. THE RANDOM PHASE APPROXIMATION

We determine the density fluctuation excitation spectrum in the RPA by means of the equation of motion method (2, 4, 5). In the present case, we are interested in finding directly the operator which creates a density fluctuation excitation of momentum  $\mathbf{q}$ . We are therefore led to study the equation of motion of the particle-hole pair operator,  $C_{p+q}^+ C_p$ . (We are suppressing spin indices in what follows.) The Hamiltonian for the system we again take to be given by

$$H = \sum_p \frac{p^2}{2m} C_p^+ C_p + \sum_q \frac{V_q}{2} (\varrho_q^+ \varrho_q - N). \quad (1.19)$$

It is then a straightforward application of the anticommutation rules for the particle operators to show that

$$\begin{aligned} [H, C_{p+q}^+ C_p] &= \omega_0(p, q) C_{p+q}^+ C_p \\ &\quad - \sum_k (V_{k/2}) \{(C_{p+q}^+ C_{p+k} - C_{p+q-k}^+ C_p) \varrho_k^+ \\ &\quad + \varrho_k^+ (C_{p+q}^+ C_{p+k} - C_{p+q-k}^+ C_p)\}. \end{aligned} \quad (1.20)$$

We see that through (1.20) a single-pair excitation is connected to a two-pair excitation; in general, we would next need to write down the equation of motion of the two-pair excitation and would find it coupled to both the one-pair and a three-pair excitation, etc. This series of coupled equations of motion represents simply another way of writing the Schrödinger equation, and is, of course, too complicated to be solved exactly.

The lowest order approximate solution of the chain of coupled equations, of which (1.20) is the first, is obtained by neglecting the particle interaction altogether. In that case, the electron-hole pair is seen to oscillate at a frequency  $\omega_0(p, q)$  in accord with the results of the preceding section. In the RPA, one continues to work only with (1.20); one further keeps only part of the interaction terms which appear on the right-hand side of that equation. The RPA consists in the following pro-

cedure: on the right-hand side of (1.20), replace the operators in parentheses by their expectation value taken over the states of the non-interacting particle system. Thus for a system at  $T = 0$ , we write, in the RPA,

$$\begin{aligned} C_{p+q}^+ C_{p+k} - C_{p+q-k}^+ C_p &\rightarrow \langle 0 | C_{p+q}^+ C_{p+k} - C_{p+q-k}^+ C_p | 0 \rangle \quad (1.21) \\ &\rightarrow (n_{p+q}^0 - n_p^0) \delta_{q,k} \end{aligned}$$

and (1.20) becomes

$$[H, C_{p+q}^+ C_p] = \omega_0(p, q) C_{p+q}^+ C_p - V_q (n_{p+q}^0 - n_p^0) \varrho_q^+. \quad (1.22)$$

The resulting operator equation (1.22), is linear in the particle-hole pair operators, so that a solution for the eigenfrequencies of the pair excitations is easily found. It should be noted that (1.22) is not the most general linear equation one can obtain: there are further linear terms in the particle-hole operators which can be extracted from products of the form

$$C_{p+q}^+ C_{p+k} \varrho_k^+.$$

As we shall see, the latter terms correspond to considering the possibility of “exchange” scattering of a particle-hole pair. In the RPA such scattering processes are neglected. What one does in the RPA is equivalent to:

- (1) Keeping *only* the term in the particle interaction associated with momentum transfer  $\mathbf{q}$ , if, as here, one is following the motion of an excitation of momentum  $\mathbf{q}$ .
- (2) Neglecting the fluctuations in the particle number  $N_p$  about its average unperturbed value,  $n_p^0$ .

The physical content of the RPA is made clear by a closer inspection of the fundamental equation, (1.22). The second term on the right-hand side of (1.22) acts as a forcing term for the motion of a particle-hole pair. It is proportional to  $V_q \varrho_q^+$ , which we can regard as an averaged force field produced by all the particles in the system. That field must, however, arise from the pair excitations; one searches therefore for a self-consistent solution of (1.22). Thus, the RPA corresponds to a time-dependent Hartree approximation, in the sense that only the “average” force field, of wave vector  $\mathbf{q}$ , associated with the particle density fluctua-

tions is retained. The terms we have neglected give rise to fluctuations about that average field, and are assumed small.

We now use (1.22) to determine the form of the operator  $\xi_p$ , which satisfies an approximate oscillatory equation of motion:

$$[H, \xi_q^+] = \omega_q \xi_q^+ \quad (1.23)$$

and so describes an elementary excitation of momentum  $q$ . Since (1.22) is linear in the particle-hole operators, it is clear that  $\xi_q^+$  is formed from the superposition

$$\xi_q^+ = \sum_p A(p, q, \omega) C_{p+q}^+ C_p. \quad (1.24)$$

Let us substitute (1.24) into (1.23). On making use of (1.22), we find

$$\begin{aligned} & \sum_p A(p, q, \omega) \{\omega_q - \omega_0(p, q)\} C_{p+q}^+ C_p \\ &= \sum_p A(p, q, \omega) \{n_p^0 - n_{p+q}^0\} V_q \varrho_q^+. \end{aligned} \quad (1.25)$$

The right-hand side of this equation consists of a constant term multiplying  $\varrho_q^+$ . In order that the left-hand side take this same form it is necessary that

$$A(p, q, \omega) = \frac{A'(q, \omega)}{\omega_q - \omega_0(p, q)}$$

where  $A'$  is a constant which is independent of  $p$ .

On making use of this result, we see that (1.25) possesses a solution only if

$$1 = V_q \sum_p \frac{n_p^0 - n_{p+q}^0}{\omega_q - \omega_0(p, q)} \quad (1.26)$$

which is the well-known RPA dispersion relation for the collective modes of an interacting fermion system.

For a repulsive interaction ( $V_q > 0$ ), as long as the condition

$$\omega_q > \omega_0(p, q) \quad (1.27)$$

is satisfied, the collective modes will be well defined, in that their energies will be distinct from those of the continuum of particle-hole pairs.

Where this condition is no longer satisfied, the dispersion relation (1.26) is not well defined. One can arrive at an appropriate prescription for treating the singularities at

$$\omega_q = \omega_0(p, q)$$

if one introduces an external forcing term into the equations of motion, (1.20), and requires that the system response be causal (follow in time the onset of the interaction between the system and the external force). The causality condition is satisfied if we everywhere make the replacement

$$\omega \rightarrow \omega + i\eta$$

where  $\eta$  is a small positive infinitesimal number. The dispersion relation, (1.26) therefore becomes

$$1 = V_q \sum_p \frac{n_p^0 - n_{p+q}^0}{\omega_q - \omega_0(p, q) + i\eta}. \quad (1.27)$$

In working with (1.27), one transforms to an integral over  $\mathbf{p}$ , and makes use of the relation (valid under the integral sign)

$$\frac{1}{\omega_q - \omega_0(p, q) + i\eta} \rightarrow \mathcal{P} \frac{1}{\omega_q - \omega_0(p, q)} - i\pi \delta[\omega_q - \omega_0(p, q)]. \quad (1.28)$$

One may ask: what is the coupling between the particle-hole excitations which is taken into account by the RPA, and which therefore gives rise to a collective mode? To answer this question we consider the scattering of a particle and hole of momentum  $\mathbf{q}$  as a consequence of the particle interaction,

$$V = \sum_{pp'q} \frac{V_q}{2} C_{p\sigma}^+ C_{p'+q'\sigma'}^+ C_{p'\sigma'}^- C_{p+q\sigma}^- \quad (1.29)$$

Let us suppose that initially we have a particle in a state of momentum  $\mathbf{p} + \mathbf{q}$ , spin  $\sigma$ , and a hole in the state  $\mathbf{p}\sigma$ . One possible consequence of the interaction is that the particle simply falls back into the hole in the Fermi sphere; the matrix element for this process is  $V_q$ ; in the process another particle-hole pair,  $(\mathbf{p}' + \mathbf{q}\sigma')$  and  $(\mathbf{p}', \sigma')$ , is created. A second

possibility is that the particle is scattered from the state  $\mathbf{p} + \mathbf{q}\sigma$  to the state  $\mathbf{p}' + \mathbf{q}\sigma$ , while the hole is scattered from a state  $\mathbf{p}\sigma$  to the state  $\mathbf{p}'\sigma$ . The matrix element for this process is  $-V_{p'-p}$ . In the first (pair annihilation) process, the new particle-hole pair may have either the same spin  $\sigma$ , or opposite spin; in the second (scattering) process, the new particle-hole pair must have the same spin,  $\sigma$ , as that of the initial pair.

Only the first, "annihilation" process, is taken into account within the RPA. The second, scattering process, involves a momentum transfer different from  $\mathbf{q}$  and is thus not included. On the other hand, in the RPA one takes into account not simply a single-pair annihilation process, but rather one sums the series of all such processes which go with the momentum transfer  $\mathbf{q}$ . The summation of the series is performed automatically when one obtains the self-consistent solution to (1.22).

It should be emphasized that the RPA is essentially an "operator" approximation, which can be carried out as easily at finite temperatures as at  $T = 0$ . At finite temperatures, the only change in the modus operandi is that in place of (1.21) one has the finite temperature analog

$$C_{p+q}^+ C_{p+k} - C_{p+q-k}^+ C_p \rightarrow \{n_{p+q}^0(T) - n_p^0(T)\} \delta_{q,k} \quad (1.30)$$

where  $n_p^0(T)$  is the unperturbed distribution function for the system at a temperature  $T$ . For an electron gas, the finite temperature analog of (1.26) in the classical limit provides the dispersion relation for the longitudinal plasma oscillations in a classical plasma.

Before going on to a consideration of particular collective modes, we wish to make two further remarks. First, we note that the pair states, specified by (1.28), continue to represent in the RPA an acceptable mode of excitation of the system, so that the continuum contribution persists, although its contribution to  $S(q, \omega)$  may be very different; second, we remark that one may, with the aid of (1.25) and (1.26), obtain an explicit construction within the RPA for the operators  $\xi_q^+$  and  $\xi_q$  which create and annihilate the density fluctuation elementary excitations (6, 7).

### E. COLLECTIVE MODES

We now investigate in further detail the character of the RPA collective modes which appear as a solution of (1.26). The summation over

momentum states in (1.27) is not, in fact, difficult to carry out. It is made even easier if, in the term proportional to  $n_{p+q}^0$ , one makes the change of the summation variable.

$$\mathbf{p} \rightarrow \mathbf{p}' - \mathbf{q}$$

so that one has in place of (1.27)

$$1 = V_q \sum_p n_p^0 \left\{ \frac{1}{\omega_q - \omega_0(p, q) + i\eta} - \frac{1}{\omega_q - \omega_0(p - q, q) + i\eta} \right\}$$

or

$$1 = \frac{q^2 V_q}{m} \sum_{p < p_F} \frac{1}{\left( \omega_q - \frac{\mathbf{q} \cdot \mathbf{p}}{m} \right)^2 - q^4/4m^2}. \quad (1.31)$$

On changing the sum to an integral, and carrying out the integral over the states within the Fermi sphere, one finds

$$1 = N(0)V_q \left\{ -1 + \frac{q_F}{2q} \left[ \left\{ \frac{(\omega_q - q^2/2m)^2}{q^2 v_F^2} - 1 \right\} \ln \left| \frac{\omega_q - qv_F - q^2/2m}{\omega_q + qv_F - q^2/2m} \right| \right. \right. \\ \left. \left. + \left\{ \frac{(\omega_q + q^2/2m)^2}{q^2 v_F^2} - 1 \right\} \ln \left| \frac{\omega_q + qv_F + q^2/2m}{\omega_q - qv_F + q^2/2m} \right| \right] \right\}. \quad (1.32)$$

The dispersion relation (1.32), appears rather formidable. However, one can obtain solutions without too much difficulty in various limiting cases of physical interest. We proceed to the discussion of the RPA collective modes for quantum and classical plasmas, and for a neutral fermion system.

### 1. Quantum Plasma Oscillations: Plasmons

We consider first the collective mode of an electron gas at  $T = 0$ . In dealing with this system, we assume that the electrons are immersed in a uniform background of positive charge, in order that the total system be neutral, and hence stable against charge density fluctuations. This system may be regarded as a quantum plasma since it represents the

$T = 0$  analog of the model used to treat electronic phenomena in classical plasmas. For the plasma, one has for the Fourier coefficients which appear in (1.26)

$$\begin{aligned} V_q &= 4\pi e^2/q^2, & q \neq 0 \\ V_q &= 0, & q \equiv 0. \end{aligned} \quad (1.33)$$

That  $V_0 = 0$  follows from the fact that the uniform background of positive charge exactly cancels the spatially uniform part of the Coulomb interaction between the electrons.

One can appreciate the essential aspects of the collective modes of the electron gas, the plasma oscillations, more readily with the aid of (1.31) rather than (1.32). Let us consider (1.31) in the limit of very long wavelengths. With the aid of (1.33), one finds that in this limit

$$\omega_q \rightarrow \omega_p = \frac{(4\pi Ne^2)^{1/2}}{m}, \quad q \rightarrow 0 \quad (1.34)$$

where  $\omega_p$  is the classical plasma frequency. Moreover, for small  $q$ , the energy of a plasmon (the quantum of plasma oscillation) varies as

$$\omega_q = \omega_p + \frac{3q^2 v_F^2}{10\omega_p} + \dots \quad (1.35)$$

as a straightforward expansion of (1.31) in powers of  $q v_F / \omega_q$  shows. Thus at long wavelengths, the plasmon is far removed from the particle-hole continuum (the maximum energy of the latter being  $q v_F + q^2/2m$ ). As one increases the wavelength, the plasmon energy increases slowly with  $q$ , according to (1.32); the maximum of the electron-hole pair continuum increases more rapidly. As a result, one arrives at a momentum,  $q_c$ , for which

$$\omega_{q_c} = q_c v_F + q_c^2/2m; \quad (1.36)$$

at this point decay of a plasmon into an electron-hole pair becomes energetically possible. [This criterion for plasmon decay was first introduced by Sawada *et al.* (6) and by Ferrell (8).]

The exact determination of the threshold wavevector from (1.36) requires the solution of the full dispersion relation (1.32). For an electron

gas at metallic densities one can obtain a satisfactory estimate of  $q_c$  from the long wavelength version of (1.36);

$$q_c \cong \omega_p/\nu_F. \quad (1.37)$$

For plasma modes with  $q > q_c$ , it becomes necessary to take into account the possibility of plasmon decay. One finds, with the aid of (1.27), that once the plasmon is able to decay into an electron-hole pair it does so readily, so that the plasmon ceases to be a well defined elementary excitation of the system for values of  $q$  only slightly greater than  $q_c$ .

The physical mechanism responsible for plasma oscillation is easily understood. Suppose there exists a charge imbalance within the plasma; the resulting space charge gives rise to an electric field which acts to oppose that charge imbalance and to bring about overall charge neutrality. Thus in response to the polarization field, the remaining electrons move into the affected area; in so doing they will overshoot the target somewhat, be pulled back, overshoot, etc. In other words, the averaged field of the electrons associated with any departure from neutrality acts as a restoring force for the collective oscillation of the system about an equilibrium state which is electrically neutral.

## 2. Classical Plasma Oscillations

We consider next the collective modes in a classical plasma. Because we are here interested in high-frequency behavior characteristic of the electrons, we use a model in which the positive ions are replaced by a uniform background of positive charge. In the classical plasma, the density and temperature of the electrons are assumed to be such that in the absence of electron-electron interaction, the electrons are characterized by a classical distribution function, which at equilibrium takes the usual Maxwellian form. Despite the great difference on the statistics of the noninteracting particles, we shall see that the collective modes in classical and quantum plasmas are remarkably similar.

As we have mentioned, it is straightforward to apply the RPA to an interacting particle system at any temperature  $T$ . The dispersion relation for the collective modes may readily be obtained from (1.27) and (1.30).

It takes the form

$$1 = \frac{4\pi e^2}{\hbar q^2} \sum_p \frac{n_p^0(T) - n_{p+\hbar q}^0(T)}{\omega_q - \left( \frac{q \cdot p}{m} + \frac{\hbar q^2}{2m} \right) + i\eta} \quad (1.38)$$

where we have included the factors of  $\hbar$  in order to facilitate passage to the classical limit. We now pass to that limit with the aid of the following relations:

$$\begin{aligned} \sum_p &\rightarrow \int d^3v \\ n_p^0(T) &\rightarrow f_0(v) \\ n_{p+\hbar q}^0(T) &\rightarrow f_0(v) + \frac{\hbar}{m} \mathbf{q} \cdot \nabla_v f_0(v) \end{aligned} \quad (1.39)$$

where  $f_0(v)$  is the Maxwellian velocity distribution at temperature  $T$ . On making the substitutions (1.39), changing from a sum over momenta  $\mathbf{p}$  to an integral over velocities, and letting  $\hbar \rightarrow 0$  wherever possible, one finds

$$1 = - \frac{4\pi e^2}{mq^2} \int d^3v \frac{\mathbf{q} \cdot \nabla_v f_0(v)}{\omega_q - \mathbf{q} \cdot \mathbf{v} + i\eta} \quad (1.40)$$

which is the dispersion relation for classical plasma oscillations.

It is straightforward to transform (1.40) into a one-dimensional integral in velocity space, since only the only direction of interest is that of  $\mathbf{q}$ . One finds then

$$1 = - \frac{4\pi e^2 N}{mq^2} \int_0^\infty dv \frac{q (\partial/\partial v) f_0(v)}{\omega_q - qv + i\eta} \quad (1.41)$$

where  $f_0(v)$  is the normalized one-dimensional velocity distribution.

$$f_0(v) = \left( \frac{1}{2\pi v_-^2} \right)^{1/2} \exp - \frac{v^2}{2v_-^2} \quad (1.42)$$

and  $v_-$ , the root mean square thermal velocity, is defined by

$$mv_-^2 = \kappa T.$$

As we have mentioned earlier, the small imaginary part,  $i\eta$ , in (1.41) arrives from a choice of retarded boundary conditions in the solution of the equations of motion. Such a solution is, in fact, valid only when  $\text{Im } \omega > 0$ , so that (1.41), as it stands cannot be used to treat damped waves, for which  $\text{Im } \omega < 0$ . In order to treat the latter, it is necessary to analytically continue the dispersion relation into the lower half of the complex plane. Such a procedure may be justified in detail by treating plasma oscillations as an initial value problem, and using the theory of Laplace transforms (9, 10). For the small rates of damping which will interest us here, the results one obtains are equivalent to the familiar prescription:

$$\frac{1}{\omega_q - q\nu + i\eta} \rightarrow \mathcal{P} \frac{1}{\omega_q - q\nu} - i\pi \delta(\omega_q - q\nu).$$

Thus we write (1.40) in the following form:

$$1 = -\frac{\omega_p^2}{q^2} \mathcal{P} \int_0^\infty d\nu \frac{q(\partial f_0/\partial\nu)}{\omega_q - q\nu} + \frac{i\omega_p^2\pi}{q^2} \int_0^\infty d\nu q(\partial f_0/\partial\nu) d(\omega_q - q\nu). \quad (1.43)$$

It is not difficult to solve (1.43) in the long-wavelength limit. In this limit, one finds  $\omega_q \gg q\nu$ ; one can therefore integrate by parts the first term on the right-hand side of (1.43), and expand the result in a power series in  $q\nu/\omega_q$ . If we write

$$\omega_q = \omega_1 + i\omega_2,$$

we find that to lowest order in  $q\nu/\omega$ , and  $\omega_2/\omega_1$  (1.43), becomes

$$1 = \frac{\omega_p^2}{\omega_1^2} + \frac{2i\omega_2\omega_p^2}{\omega_1^3} - i \sqrt{\frac{\pi}{2}} \frac{\omega_p^2}{q^2\nu_-^2} \frac{\omega_1}{q\nu_-} \exp - \frac{\omega_1^2}{2q^2\nu_-^2} \quad (1.44)$$

which possesses the solution

$$\begin{aligned} \omega_1 &= \omega_p \\ \frac{\omega_2}{\omega_p} &= \sqrt{\frac{\pi}{8}} \frac{\omega_p^2}{q^2\nu_-^2} \frac{\omega_p}{q\nu_-} \exp - \frac{\omega_p^2}{2q^2\nu_-^2} \end{aligned} \quad (1.45)$$

These results were first obtained by Landau (9) and by Bohm and Gross (11).

We see from (1.45) that to lowest order in  $q$  the classical plasma wave has the same frequency as that found for the quantum plasma. On the other hand, the classical plasma wave is damped. From a quantum point of view this damping, the so-called Landau damping, occurs because at finite temperatures the continuum of particle-hole pair excitations is spread out over the entire energy spectrum, rather than being cut off at  $q\nu_F$ . As a result, there is always a slight probability of finding a particle in the tail of the Fermi-Dirac (or Maxwellian) distribution function which is capable of absorbing energy from the plasma wave. From a classical point of view, the damping is to be attributed to particles which move in phase with the collective mode, that is, particles with velocity  $v$  such that

$$\frac{\mathbf{q} \cdot \mathbf{v}}{q} = \frac{\omega_p}{q} = v_{ph} \quad (1.46)$$

where  $v_{ph}$  is the phase velocity of the plasma wave.

In order to observe a damping of the plasma wave, two conditions must be fulfilled: first, there must be single particles in the plasma which are capable of exchanging momentum and energy with the plasma wave; second, the number of particles with velocities *less* than the phase velocity of the plasma wave must be *greater* than the number of particles which have velocities greater than the phase velocity of the plasma wave. Particles with velocities (in the direction of the wave) less than  $v_{ph}$  absorb energy from the wave, while those with velocities greater than  $v_{ph}$  give up energy to it. [This may easily be seen if one transforms to a system of coordinates moving with the phase velocity of the plasma wave (11).] Thus, if  $f(\mathbf{v})$  is the electron velocity distribution where

$$\mathbf{q} \cdot \nabla_v f(\mathbf{v}) < 0. \quad (1.47)$$

We find damping, as for the case of the Maxwellian distribution we have considered. On the other hand, if

$$\mathbf{q} \cdot \nabla_v f(\mathbf{v}) > 0 \quad (1.48)$$

(which means a velocity distribution with two humps) one may have

a growing plasma wave, depending on the exact location of the second hump. If some plasma waves are unstable, the RPA description of the plasma becomes inapplicable, and one must take into account various nonlinear effects in the coupling between the waves and the particles.

For the Maxwellian velocity distribution, at long wavelengths the Landau damping is essentially negligible; there are very few particles which possess velocities equal to  $\omega_q/q$ . On the other hand, once the phase velocity of the plasma wave is comparable to the mean thermal particle velocity, that is, for

$$q \cong q_D = \frac{\omega_p}{v_{\perp}}, \quad (1.49)$$

there is no lack of particles to absorb energy from the plasma wave, and one expects, and finds, that the plasma oscillation is strongly damped. For the classical plasma, then,  $q_D$  represents the maximum wave vector for which it is useful to regard the plasma oscillation as a well-defined collective mode of the system. The reader may note the close resemblance between the limiting wave vectors for the quantum and classical plasmas (1.37) and (1.49).

### 3. Zero Sound

We consider now the density fluctuation collective mode for a neutral fermion system. We shall confine our attention to the long-wavelength limit of the zero temperature dispersion relation. As long as the interaction is well behaved (i.e., falls off more rapidly in space than the coulomb interaction),

$$\lim_{p \rightarrow 0} V_q \rightarrow V$$

where  $V$  is a constant. The solution of (1.31) or (1.32) is then straightforward in both the strong coupling and weak coupling limits.

For strong coupling, one can, as for the plasmons, expand (1.31) in powers of  $q \cdot v_F/\omega_q$ ; one finds, in lowest order

$$\omega_q = \frac{(NV)^{1/2}}{(m)^{1/2}} q \quad (1.50)$$

provided the sound velocity,  $(NV/m)^{1/2}$ , is large compared to the velocity of a particle on the Fermi surface,  $\nu_F$ . This criterion is equivalent to the criterion

$$N(0)V \gg 1 \quad (1.51)$$

where  $N(0)$  is the density of states per unit energy for particles of one kind of spin (1.17).

In the opposite limit, of weak coupling, for which

$$N(0)V \ll 1 \quad (1.52)$$

it is convenient to make use of the dispersion relation (1.32). We first note that the frequency of the collective mode must be very nearly equal to  $q\nu_F$ , since it is only for such values that the logarithmic terms yield a contribution of order  $1/N(0)V$ , and a solution of the dispersion relation can be found. If we introduce the parameter

$$\lambda = \frac{\omega_q}{q\nu_F}, \quad (1.53)$$

(1.32) reduces to the relation

$$\lambda \ln \left| \frac{\lambda + 1}{\lambda - 1} \right| = \frac{1}{N(0)V} + 2 \quad (1.54)$$

to terms of lowest order in  $q$  and  $N(0)V$ . One finds then

$$\lambda = 1 + \left( \frac{2}{e^2} \right) \exp - 1/N(0)V$$

or

$$\omega_q = q\nu_F \left\{ 1 + \left( \frac{2}{e^2} \right) \exp - 1/[N(0)V] \right\} \quad (1.55)$$

as the dispersion relation for zero sound. In the weak coupling limit, then, the collective mode sits just above the continuum of particle-hole pair excitations.

In general, in the long-wavelength limit of the RPA, there will exist

a zero sound mode which is distinct from the particle-hole excitation spectrum no matter what the coupling constant  $V$  might be (again as long as  $V$  is positive, corresponding to a repulsive interaction between the particles). As the wave vector of the collective mode increases, one finds a critical wavevector,  $q_c$ , at which the collective mode merges with the continuum of particle-hole excitations. The spectra merge because the maximum pair excitation energy

$$\frac{q v_F}{m} + \frac{q^2}{2m}$$

increases more rapidly with  $q$  than does the energy of the collective mode, as a result of the  $q^2$  dependence of the former. Just what value  $q_c$  takes is a matter for detailed calculation. For example, in the case of weak coupling, one finds directly from (1.32) that

$$q_c = \frac{2}{e} p_F \exp - \frac{1}{N(0)V}. \quad (1.56)$$

Just as for the plasmons, once it becomes possible for a zero sound mode to decay into a particle-hole pair, the collective mode is strongly damped by single pair excitation, and ceases to be a well-defined elementary excitation of the system. In the weak coupling case, the range of wave vectors for which zero sounds exists is seen to be very small indeed.

#### 4. Zero Sound versus First Sound

The collective modes we have considered resemble sound waves, in that they correspond to a longitudinal oscillation of the particle density. Their physical origin is, however, quite different. An ordinary, or first, sound wave is a hydrodynamic phenomenon. It occurs under conditions such that the system displays local thermodynamic equilibrium, as a consequence of frequent short-range collisions between the system particles. As a result, when the particle density increases in a certain region, a pressure wave is set up which acts to restore the local equilibrium conditions. For hydrodynamic concepts to apply, the particles must suffer many collisions during a period of oscillation of the sound wave. One

therefore expects to find a first sound wave for frequencies  $\omega$  and collision times  $\tau$  such that

$$\omega\tau \ll 1. \quad (1.57)$$

In the case of the collective modes, such as plasma oscillation and zero sound, the restoring force on a given particle is the average time-dependent self-consistent field of all the other particles. That this is the case is perhaps obvious for the plasmons; it is equally true for zero sound, as may be seen from an inspection of the equation of motion for a particle-hole pair (1.21). The restoring force for the collective mode appears on the right-hand side of that equation; it is the averaged density field of all the other particles. The short-range collisions between the individual particles act to disrupt the effect of that averaged field, and therefore serve to damp the collective mode.

Consider, for example, a long-wavelength collective mode in a fermion system at  $T = 0$ . Within the RPA it is not damped, since Landau damping is forbidden by energy and momentum conservation. Beyond the RPA, however, one takes into account a coherent superposition of "dressed" pair states, in which each component may consist of a "dressed" quasi particle. The "dressed" quasi-particle states possess a finite lifetime; so will the collective mode. Such damping of the collective mode may be regarded as arising from a coupling of the mode to configurations involving two particles and two holes, since a damped quasi particle exists, in part, as a particle, plus a particle-hole pair. Roughly speaking, the criterion that a collective mode exist will be

$$\omega\tau \gg 1 \quad (1.58)$$

where  $\tau$  as above, represents the collision time for the particles.

At a temperature  $T$  such that

$$\varkappa T \ll E_F$$

the collision time, as a consequence of the Pauli principle phase-space restrictions, varies with temperature as

$$\tau = AT^2.$$

At low temperatures then, such collision damping, like the Landau damp-

ing, is totally ineffective in damping the plasma waves of frequency near  $\omega_p$ . Matters are otherwise for the zero sound waves. Indeed at a given temperature  $T$ , since the zero sound frequency is proportional to  $q$ , at very long wavelengths the condition (1.58) is not satisfied, but instead (1.57) applies. Hence at very long wavelengths one has first sound waves. Then, as one passes to shorter wavelengths, one passes to the zero sound regime (assuming the temperature is sufficiently low). The transition between the two regimes is undoubtedly smooth, but is complicated to work out in any detail, since one is working in a domain where neither the hydrodynamic or the collective mode description is strictly valid.

#### F. SUMMARY

In this lecture we have tended to focus our attention on a particular class of pair excitations, the density fluctuations, and on a particular approximation, the RPA. Just as the density fluctuations represent the system response to an external beam, so too can one find the appropriate pair excitations which determine the response to an arbitrary external probe. Such pair excitations are all of the form [cf. (1.24)],

$$\xi_q^+ = \sum_{\substack{p \\ \sigma, \sigma'}} A(p, q, \omega) C_{p+q\sigma}^+ C_{p\sigma'}. \quad (1.59)$$

Depending on the choice of the coefficients  $A_{\sigma\sigma'}(p, q, \omega)$ , one deals with a transverse current density fluctuation, a spin density fluctuation, etc. In any given case, one may attempt, by methods quite similar to those employed here, to determine whether in addition to the continuum of pair excitations, collective modes may exist, and, if so, what their character might be.

How good is the RPA? From the way in which we have derived the collective modes, it is clear that the effects of the interaction between the particles are regarded as essentially weak, since we have inserted the unperturbed particle distribution functions into the basic dispersion relation. We have as well neglected a large class of terms in the perturbation-theoretic expansion of the particle interaction energy by confining our attention to the first of the infinite set of coupled equations. The detailed study of the validity of the RPA lies beyond the scope of this

lecture; we may quote, however, the results of such studies for classical and quantum plasmas. For both systems, the RPA is valid provided:

$$\frac{\langle V \rangle}{\langle T \rangle} \ll 1. \quad (1.60)$$

Here  $\langle V \rangle$  is the average potential energy of interest, while  $\langle T \rangle$  is the average kinetic energy of interest.

For the classical plasma, the criterion (1.60) becomes

$$\frac{e^2}{r_0} \ll \kappa T \quad (1.61)$$

a criterion which is well satisfied for classical plasmas of physical interest, ranging from the ionosphere, through the conduction electrons and holes in semiconductors, to the "hot" laboratory plasmas of interest for controlled fusion research. It should be recalled that, as we have mentioned, the RPA does fail when the electron velocity distribution is such that one encounters growing plasma waves.

For the quantum plasma, the criterion for validity of the RPA becomes

$$r_0 \ll (\hbar^2/me^2) \quad (1.62)$$

a requirement which limits its validity to electron gases of a density some ten times higher than that encountered in the conduction band of metals. As we shall see in a subsequent lecture, improvements in the RPA do not alter the plasma dispersion relation in the long-wavelength limit. Thus one finds in general for the plasmon energy,

$$\omega_q = \omega_p + (a + ib) q^2 + \dots$$

where the coefficients  $a$  and  $b$  differ from their RPA values.

The correct description of the longitudinal collective modes for a neutral fermion system requires the use of the Landau Fermi liquid theory. In certain limiting cases, the results of that theory take the form of the RPA result (3.49). In such cases, however,  $V$  is replaced by the effective scattering amplitude for a pair of quasi particles [see, for example, Nozieres (12)].

Our discussion of the dynamic form factor for fermion systems at  $T = 0$  may be summarized in the following way. For a neutral system, there are essentially three regimes of interest:

$$(i) \quad q < q_c \ll q_F.$$

Here the collective mode is well defined and is seen superposed on the weak continuum contribution associated with configurations involving two quasi-particle and quasi-hole excitations, three quasi-particle and quasi-hole excitations, etc. The continuum contribution, associated with configurations involving a quasi-particle, quasi-hole pair, is found below  $\omega \approx qv_F$ .

$$(ii) \quad q_c \lesssim q \ll q_F.$$

The collective mode has merged with the quasi-particle, quasi-hole pair excitation spectrum. A sharp well-defined peak in  $S(q, \omega)$  no longer exists. There is, however, a definite piling up of states in the vicinity of  $\omega \approx qv_F$  since the pair excitations continue to give the dominant contribution to  $S(q, \omega)$ .

$$(iii) \quad q_c \ll q \approx q_F.$$

The dominant configurations which contribute to  $S(q, \omega)$  no longer consist simply of a quasi particle and a quasi hole. Contributions from configurations involving a number of quasi particles and quasi holes play an equally important role. There is little or no structure in  $S(q, \omega)$ .

For an electron gas at metallic densities the dynamic form factor behaves in qualitatively the same way. The essential difference is that because  $\omega_p$  is somewhat larger than the Fermi energy,  $q_c$  is comparable to  $q_F$ . As a result one goes almost at once from region (i) to region (iii). There is no well-defined region (ii).

## II. Correlation and Response for Neutral Systems

### A. DENSITY-DENSITY RESPONSE FUNCTION AT $T = 0$

In the first part of these lectures we have considered the resonant transfer of energy and momentum from a beam of particles to a many-particle system. The particle beam represents an example of a time-

and space-varying longitudinal probe of system behavior; longitudinal because it couples directly to a longitudinal excitation mode, the density fluctuations. For a system in its ground state, the dynamic form factor serves to specify the "out-of-phase" response of the system to an external longitudinal probe. Then will also be an "in-phase" response, which corresponds to a polarizability of the system; generally one is interested in the complete density-density response function, which includes both the "in-phase" and "out-of-phase" response of the system density fluctuations to a weak longitudinal probe. Because the response of the system is causal (that is, follows in time the onset of the probe-system coupling), one has a set of Kramers-Kronig relations which relate the in-phase and out-of-phase parts of the response function. Hence the dynamic form factor serves to determine completely the overall density-density response function, as we shall now demonstrate.

We begin, as in Section I, B, with the consideration of a time-varying longitudinal probe which is coupled directly to the density fluctuations of the system. Such a coupling may be expressed by an interaction Hamiltonian of the form

$$H_{\text{ext}} = \sum_q \frac{\int_{-\infty}^{\infty} d\omega \mathcal{V}_q}{2\pi} \varrho_q^+ \varrho_e(q, \omega) \exp(-i\omega t) \quad (2.1)$$

where  $\varrho_e(q, \omega)$  is the Fourier transform in space and time of the probe particle density and  $\mathcal{V}_q$  is the Fourier transform in space of the potential energy of interaction between the probe and the system. Since the perturbing field must be real, the Fourier components of  $\varrho_e$  must satisfy the relation  $\varrho_e(q, \omega) = \varrho_e(-q, -\omega)$ . For the external particle considered in Section I, A, one has

$$\varrho_e(q, \omega) = \exp(-i\mathbf{q} \cdot \mathbf{R}_e) \delta(\omega - q \cdot \mathbf{P}_e / M_e) \quad (2.2)$$

in the approximation in which the recoil of the scattered particle can be neglected.

We have not specified any boundary conditions in (2.1), that is the time at which the interaction,  $H_{\text{ext}}$ , between the probe and the system should be regarded as beginning. One has a certain liberty in the choice of boundary conditions; however, by far the most convenient is that choice which corresponds to turning on the interaction adiabatically, at

some time in the distant past, and then studying the response of the system. In this way, one avoids heating up the system by a substantial transfer of energy from the probe to the system; one also ensures that the system response shall be causal. The use of adiabatic and causal boundary conditions is equivalent to the mathematical statement that

$$H_{\text{ext}} = \lim_{\eta \rightarrow 0} \sum_q \int_{-\infty}^{\infty} d\omega \mathcal{V}_q \varrho_q^+ \varrho_e(q, \omega) \exp(-i\omega t) \exp(\eta t) \quad (2.3)$$

we shall verify that this is indeed the case in the course of our subsequent calculations; note that  $H_{\text{ext}}$  vanishes in the distant past, at  $t = -\infty$ , it then slowly increases in strength until it reaches its full value (2.1), at  $t = 0$ . As we have emphasized, we are interested in a probe which is weakly coupled to the system. Thus each Fourier component of the probe density acts independently; a given  $\varrho_e(q, \omega)$  induces its own density fluctuation of the system particles with wave vector and frequency  $\pm (q, \omega)$ . We define the retarded density-density response function,  $\chi(q, \omega)$ , as follows:

$$\chi(q, \omega) = \frac{\langle \varrho(q, \omega) \rangle}{\mathcal{V}_q \varrho_e(q, \omega)}. \quad (2.4)$$

Here  $\langle \varrho(q, \omega) \rangle$  is the Fourier transform in space and time of the expectation value of the average density fluctuation,  $\langle \varrho(r, t) \rangle$  induced by the perturbing potential (2.3). We have included the potential,  $\mathcal{V}_q$ , in the definition (2.4), in order that the response function,  $\chi(q, \omega)$ , depend only on the system properties.

We calculate  $\chi(q, \omega)$  by using time-dependent perturbation theory to compute the change in the system wave function brought about by  $H_{\text{ext}}$ , under the assumption that the system is initially in its ground state. As we have remarked, in calculating  $\langle \varrho(q, \omega) \rangle$  it suffices to keep only those terms in  $H_{\text{ext}}$  which are proportional to  $\varrho_e(q, \omega)$  and its complex conjugate. The calculation proceeds as follows.<sup>3</sup> We consider the time-dependent Schrödinger equation

$$ih \frac{\partial}{\partial t} \Psi(t) = (H + H_{\text{ext}}) \Psi(t) \quad (2.5)$$

<sup>3</sup> We follow closely the treatment given by Nozières and Pines (13). For a general discussion of linear response functions, see, for example, Kubo (14).

where  $H$  is the system Hamiltonian (1.19), and  $H_{\text{ext}}$  is given by (2.3). We solve (2.5) by expanding  $\Psi(t)$  in terms of the exact many-body eigenstates,  $|n\rangle$ , of the many-particle system, the latter being defined by

$$H |n\rangle = E_n |n\rangle \quad (2.6)$$

with the  $E_n$  representing, as before, the corresponding exact system excitation energies. Thus

$$\Psi(t) = \sum_n a_n(t) |n\rangle \exp(-iE_n t) \quad (2.7)$$

where, according to our boundary conditions,

$$\begin{aligned} a_0(t = -\infty) &= 1 \\ a_n(t = -\infty) &= 0 \quad (n \neq 0). \end{aligned}$$

On substituting (2.7) into (2.6), and keeping only the terms proportional to  $\varrho_e(q, \omega)$  in  $H_{\text{ext}}$ , one finds readily

$$\begin{aligned} a_n(t) &= -\mathcal{V}_q \frac{\varrho_e(q, \omega) (\varrho_q^+)_n \exp[-i(\omega + \omega_{n0} + i\eta)t]}{\omega - \omega_{n0} + i\eta} \\ &\quad - \frac{\varrho_e^+(q, \omega) (\varrho_q)_n \exp[i(\omega + \omega_{n0} - i\eta)t]}{\omega + \omega_{n0} - i\eta} \end{aligned} \quad (2.8)$$

where the  $(\varrho_q^+)_n$  and  $\omega_{n0}$  have the same meaning as in the previous lecture.

In calculating  $\langle \varrho_q(t) \rangle$ , it suffices to keep only those terms proportional to  $\varrho_e(q, \omega)$ ; thus one has

$$\langle \varrho_q(t) \rangle = \sum_n \{(\varrho_q)_n a_n(t) \exp[-i\omega_{n0}t] + a_n^+(t) (\varrho_q)_n \exp[i\omega_{n0}t]\} \exp(-\eta t) \quad (2.9)$$

since  $\langle 0 | \varrho_q(t) | 0 \rangle$  vanishes for a translationally invariant system. The calculation of  $\langle \varrho_q(t) \rangle$  is simplified if one notes that when an intermediate state,  $|n\rangle$ , is coupled to the ground state by  $\varrho_q$ , then that same state cannot be coupled to  $|0\rangle$  by  $\varrho_q^+$ . One finds, by direct substitution

$$\langle \varrho_q(t) \rangle = -\mathcal{V}_q \varrho_e(q, \omega) \exp[-i(\omega + i\eta)t] \sum_n \frac{|(\varrho_q^+)_n|^2}{\omega - \omega_{n0} + i\eta} - \frac{|(\varrho_q)_n|^2}{\omega + \omega_{n0} + i\eta}. \quad (2.10)$$

Making use of time-reversal invariance, we may associate to each state,  $|n\rangle$ , with momentum  $\mathbf{q}$ , another state,  $|m\rangle$ , degenerate with,  $|n\rangle$ , having a momentum  $-\mathbf{q}$  and a complex conjugate wave function. Hence one has

$$\sum_n \frac{|\langle \varrho_q \rangle_{n0}|^2}{\omega + \omega_{n0} + i\eta} = \sum_m \frac{|\langle \varrho_q^+ \rangle_{m0}|^2}{\omega + \omega_{m0} + i\eta}. \quad (2.11)$$

With the aid of (2.10) and (2.11), one finds readily that

$$\chi(q, \omega) = \sum_n |\langle \varrho_q^+ \rangle_{n0}|^2 \left\{ \frac{1}{\omega - \omega_{n0} + i\eta} - \frac{1}{\omega + \omega_{n0} + i\eta} \right\} \quad (2.12)$$

which is our desired result.

We consider next various formal properties of our response function,  $\chi(q, \omega)$ . First, we remark that there is a close relationship between  $\chi(q, \omega)$  and  $S(q, \omega)$ , as we have anticipated. On comparing (2.12) with (1.9), we note that we can write

$$\chi(q, \omega) = \int_0^\infty d\omega' S(q, \omega') \left\{ \frac{1}{\omega - \omega' + i\eta} - \frac{1}{\omega + \omega' + i\eta} \right\} \quad (2.13)$$

in which form we see that  $S(q, \omega')$  represents the spectral density for  $\chi(q, \omega)$ , and serves to determine it completely. We see too that  $\chi(q, \omega)$  is analytic in the upper half of the complex  $\omega$  plane, as we should expect from our causal boundary conditions.

It is also not difficult to obtain an explicit expression for the space-time polarizability,

$$\chi(r, t) = \sum_q \int_{-\infty}^\infty \frac{d\omega}{2\pi} \chi(q, \omega) \exp i(\mathbf{q} \cdot \mathbf{r} - \omega t). \quad (2.14)$$

It is left as a problem for the reader to show that  $\chi(r, t)$  is a retarded commutator of density fluctuations taken at different times,

$$\chi(r, t) = -i \langle 0 | [\varrho(r, t), \varrho(0, 0)] | 0 \rangle \Theta(t) \quad (2.15)$$

where

$$\begin{aligned} \Theta(t) &= 1, & t > 0 \\ &= 0, & t < 0. \end{aligned} \quad (2.16)$$

In (2.15), the operators and wave functions are specified in the Heisenberg representation.

## B. SUM RULES FOR THE DYNAMIC FORM FACTOR

### 1. Current Conservation: *f*-Sum Rule

The dynamic form factor,  $S(q, \omega)$ , obeys a useful sum rule,

$$\int_0^\infty d\omega \omega S(q, \omega) = Nq^2/2m \quad (2.17)$$

where  $m$  is the mass of the system particles.<sup>4</sup> The sum rule (2.17) is equivalent to a generalized longitudinal version of the Thomas-Reiche-Kuhn sum rule for atomic spectra; it may also be expressed as a sum over oscillator strengths for the density fluctuation excitations,

$$f_{0n} = -\frac{2m}{q^2} \omega_{n0} |(\varrho_q^+)_n|^2 \quad (2.18)$$

in which form it reads

$$\sum_n f_{0n} = N = \sum_n \frac{2m}{q^2} \omega_{n0} |(\varrho_q^+)_n|^2. \quad (2.19)$$

The equivalence of (2.19) with (2.17) follows directly from the definition of  $S(q\omega)$ .

To derive (2.19) we consider the double commutator

$$[[\varrho_q, H], \varrho_q^+] \quad (2.20)$$

evaluated in two different ways. In (2.20),  $H$  is, as usual, the Hamiltonian for the interacting particle system. We assume that the potential energy of interaction between the particles is independent of their velocity; in that case, the density fluctuation,  $\varrho_q$ , commutes with the

<sup>4</sup> The sum rule, in essentially this form, was obtained by Placzek (15), in connection with the theoretical description of neutron-scattering experiments. The form (2.19) for a many-particle system, was independently derived by Pines (16), and Nozières and Pines (17). The derivation presented here is that of ref. (17).

potential energy (since that depends only on the interparticle spacing). Hence we can write

$$\begin{aligned} [\varrho_q, H] &= [\varrho_q, \sum_i p_i^2/2m] \\ &= \frac{1}{2} \sum_i \left\{ \frac{\mathbf{q} \cdot \mathbf{p}_i}{m} \right\} \exp(-i\mathbf{q} \cdot \mathbf{r}_i) + \exp(-i\mathbf{q} \cdot \mathbf{r}_i) \left\{ \frac{\mathbf{q} \cdot \mathbf{p}_i}{m} \right\} \end{aligned} \quad (2.21)$$

and

$$[(\varrho_q, H), \varrho_q^+] = \frac{q^2 N}{m}. \quad (2.22)$$

Let us now take the expectation value of (2.22) for the ground state, and, further, insert a complete set of eigenstates of the Hamiltonian  $H$  in the double commutator (2.22). We have then

$$\begin{aligned} \sum_n \{ \langle 0 | [\varrho_q, H] | n \rangle \langle n | \varrho_q^+ | 0 \rangle \\ - \langle 0 | \varrho_q^+ | n \rangle \langle n | [\varrho_q, H] | 0 \rangle \} = \frac{Nq^2}{m}. \end{aligned} \quad (2.23)$$

Further,

$$[\varrho_q, H]_{0n} = (E_n - E_0) (\varrho_q)_{0n} = \omega_{n0} (\varrho_q)_{0n} \quad (2.24)$$

since we have chosen the states  $n$  such that

$$H | n \rangle = E_n | n \rangle.$$

Equation (2.23) may therefore be written as

$$\sum_n \omega_{n0} | (\varrho_q^+)_n |^2 + \omega_{n0} | (\varrho_q)_n |^2 = \frac{Nq^2}{m}. \quad (2.25)$$

Again making use of time-reversal invariance, we may write

$$\sum_n (\omega_{n0}) | (\varrho_q^+)_n |^2 = \sum_m (\omega_{m0}) | (\varrho_q)_m |^2 \quad (2.26)$$

whence (2.19) and (2.17) follow directly from (2.25).

The sum rules are closely related to the law of current conservation for a system of particles interacting via a velocity-independent potential.

The current density,  $j(r)$ , is defined as

$$j(r) = \frac{1}{2} \sum_i \frac{\mathbf{p}_i}{m} \delta(\mathbf{r} - \mathbf{r}_i) + \delta(\mathbf{r} - \mathbf{r}_i) \frac{\mathbf{p}_i}{m}. \quad (2.27)$$

It possesses the Fourier transform,

$$j_q = \frac{1}{2} \sum_i (\mathbf{p}_i \exp[-i\mathbf{q} \cdot \mathbf{r}_i] + \exp[-i\mathbf{q} \cdot \mathbf{r}_i] \mathbf{p}_i). \quad (2.28)$$

On comparing (2.28) and (2.21), we see that (2.21) is simply the Fourier transform of an operator statement of longitudinal current conservation,

$$\dot{\varrho}_q = -[\nabla \cdot \mathbf{j}(r)]_q \quad (2.29)$$

Let us take the matrix element of (2.21) and (2.29) between the ground state  $|0\rangle$ , and an eigenstate,  $|n\rangle$ , of  $H$ , viz,

$$\omega_{n0}(\varrho_q)_{n0} = (\mathbf{q} \cdot \mathbf{j}_q)_{n0}. \quad (2.30)$$

We see that the requirement of longitudinal current conservation is equivalent to our longitudinal  $f$ -sum rule, since (2.21) and (2.30) are essential intermediate steps in the derivation of the latter.

## 2. The Compressibility Sum Rule for $S(q, \omega)$

In the long-wavelength limit, the static response function,  $\chi(q, 0)$ , is simply related to the isothermal compressibility for an uncharged many-particle system. (The corresponding relation for an electron gas will be considered in Section III of this chapter.) To obtain the relation, we remark that, in this limit, the external potential,

$$\delta V(\mathbf{r}) = \lim_{q \rightarrow 0} \mathcal{V}_q \varrho_e(q, 0) \exp(i\mathbf{q} \cdot \mathbf{r}) \quad (2.31)$$

is balanced by a pressure distribution,  $\delta\varrho(r)$ , such that

$$\delta\varrho = -N \delta V \quad (2.32)$$

where  $N$  is the equilibrium density of particles. The additional pressure,  $\delta\varrho(r)$ , will in turn change the density,  $\delta\varrho(r)$ , by an amount

$$\delta\varrho = \kappa N \delta P \quad (2.33)$$

where  $\kappa$  is the isothermal compressibility (if one considers the response at a finite temperature). On making use of (2.31-2.33), and the definition (2.4) of  $\chi(q, 0)$ , we find

$$\lim_{q \rightarrow 0} \chi(q, 0) = -\kappa N^2 = -N/ms^2 \quad (2.34)$$

where  $s$  is the macroscopic isothermal sound velocity. We have, moreover, an explicit expression for  $\chi(q, 0)$  in (2.13); it is

$$\chi(q, 0) = -2 \int_0^\infty d\omega' \frac{S(q, \omega')}{\omega'} . \quad (2.35)$$

If we now combine the expressions (2.34) and (2.35) we obtain a very useful sum rule for the long-wavelength behavior of the dynamic form factor.<sup>5</sup> We find

$$\lim_{q \rightarrow 0} \int_0^\infty d\omega \frac{S(q, \omega)}{\omega} = \frac{N}{2ms^2} . \quad (2.36)$$

We shall have occasion to make use of (2.36) in connection with our study of the density fluctuation excitation spectrum in superfluid systems.

### 3. The Static Form Factor

The dynamic form factor is the Fourier transform in space and time of the density-density correlation function,  $S(r, t)$ . Thus one has

$$S(r, t) = \sum_q \int_0^\infty d\omega S(q, \omega) \exp [i(\mathbf{q} \cdot \mathbf{r} - \omega t)] = \langle 0 | \varrho(r, t) \varrho(0, 0) | 0 \rangle \quad (2.37)$$

where the operators and wave functions are specified in the Heisenberg representation. It furnishes a measure, therefore, of the correlation between the system density at difference space-time points, as was first emphasized by van Hove (21). Another quantity of interest is the static density-density correlation function,  $S(r, 0)$ , which measures den-

<sup>5</sup> The compressibility sum rule was perhaps first obtained by L. P. Kadanoff and P. C. Martin in 1958 (18). It has been rederived independently by Mermin (19) and by Nozières (12) and Pines (20).

sity correlations at the same time. The static form factor,  $S(q, 0)$  is simply the Fourier transform of  $S(r, 0)$ . One finds

$$S(q, 0) = \int dr \exp(-iq \cdot r) S(r, 0) = \langle 0 | \varrho_q^+ \varrho_q | 0 \rangle. \quad (2.38)$$

Thus  $S(q, 0)$  furnishes a direct measure of the mean square density fluctuation in the ground state. It is frequently convenient to work with  $S_q$ , which we define as

$$S_q = \left( \frac{1}{N} \right) \langle 0 | \varrho_q^+ \varrho_q | 0 \rangle. \quad (2.39)$$

It follows directly that the “zeroth” moment of  $S(q, \omega)$  is related to  $S_q$  by

$$\int_0^\infty d\omega S(q, \omega) = NS_q. \quad (2.40)$$

### C. THE DYNAMIC FORM FACTOR FOR SUPERFLUID SYSTEMS

The sum rules (2.17) and (2.36), provide a valuable check on the consistency of a given calculation of the dynamic form factor for many-particle systems. Obviously the two moments of  $S(q, \omega)$  which these rules supply cannot in general serve to specify  $S(q, \omega)$ . There are, however, two special cases of considerable interest for which the sum rules do, in fact, determine the exact form of  $S(q, \omega)$  in the long-wavelength limit. One is that of liquid He II (or, in fact, any system of interacting bosons). The second is that of a neutral fermion system with “s” state attractive interactions. In both cases the “continuum” contribution to the dynamic form factor is negligible in the long-wavelength limit. What remains is a collective mode contribution; the sum rules then tell us that the long-wavelength collective modes are phonons whose velocity is simply the isothermal sound velocity of the system in question.<sup>6</sup> We shall thus find

$$\lim_{q \rightarrow 0} S(q, \omega) = \frac{Nq}{2ms} \delta(\omega - sq) \quad (2.41)$$

where  $s$  is the macroscopic isothermal sound velocity.

<sup>6</sup> For liquid He II, the demonstration presented here is due to Miller *et al.* (22) and to Pines (20).

### 1. Liquid He II

The dynamic form factor for a system of interacting bosons differs in an essential way from that for fermions. The difference arises from the condensed state for the boson system. Consider, first, a system of noninteracting bosons. The ground state of the system is that in which all the particles have momentum zero. If we introduce an extra particle of momentum  $\mathbf{q}$ , it will have an energy

$$\varepsilon_q = \frac{q^2}{2m}.$$

On the other hand, if we create a density fluctuation of momentum  $\mathbf{q}$ , we do so by taking a particle from the condensed state and giving it a momentum  $\mathbf{q}$ . The energy of the density fluctuation excitation mode is again  $\varepsilon_q$ ; a simple calculation shows that

$$S_0(q, \omega) = N \delta\left(\omega - \frac{q^2}{2m}\right). \quad (2.42)$$

For the noninteracting system, the density-fluctuation excitations consist exclusively of single particle excitations of a well-defined energy. Put another way, the quasi-particle excitation spectrum and the density fluctuation excitation spectrum are identical; up to terms of order  $(1/N)$  it makes no difference whether one brings a particle in from outside, or excites a particle from the condensed state.

Let us now turn on adiabatically the interaction between the bosons. We can now make an argument for the form of the quasi-particle spectrum which is analogous to that used by Landau for an interacting fermion system. We assume there is a one-to-one correspondence between the states of the interacting system and those of the noninteracting system. In that case the state with one extra boson of momentum  $\mathbf{q}$  transforms adiabatically to a state in which there is present a single quasi particle, of momentum  $\mathbf{q}$ , and energy  $\omega_q$ . (This may be expected to hold provided the life-time of the quasi particle is sufficiently long, a condition difficult to make precise for a general system of interacting bosons, but one which is known experimentally to be satisfied for the excitations of momentum  $\mathbf{q} \leq 2.7 \text{ \AA}^{-1}$  in liquid He II.)

We next remark that when we consider the density fluctuation excitation spectrum for the interacting boson system, there will be a part of that spectrum which corresponds to exciting a single quasi particle from the condensed state. What is required of the interacting boson system is simply that some finite fraction,  $N_0/N$ , of the particles remain in the condensed state, a fraction such that the number of particles in the condensed state,  $N_0$ , be large compared to unity. [For a system of macroscopic size, that fraction,  $N_0/N$ , can be very small indeed ( $\sim 10^{-15}$ , say) and one would still have  $N_0 \gg 1$ ]. In other words there must be some "vestige" of the original completely occupied condensed state, but that vestige does not have to be very sizable. The energy of the excitation will be identical to that of the corresponding quasi particle; thus there continues to be an overlap between the quasi particle spectrum and the density fluctuation excitation spectrum. We are essentially arguing that when we start with the system of  $N - 1$  "bare" particles plus one "bare" particle of momentum  $\mathbf{q}$ , on turning on the interaction we arrive, in part, at a state with a single quasi particle of momentum  $\mathbf{q}$ , energy  $\omega_q$ . The overlap need not be complete; thus one can also form a density fluctuation of momentum  $\mathbf{q}$  from excited state configurations which involve two quasi particles, three quasi particles, etc.

We therefore write

$$S(q, \omega) = NZ_q \delta(\omega - \omega_q) + S^{(1)}(q, \omega). \quad (2.43)$$

In (2.43) the first term on the right-hand side represents the contribution from excitation of a single quasi-particle (of momentum  $q$ , energy  $\omega_q$ ), while the second represents the contribution from excited state configurations involving two or more quasi-particles. Consider now the character of

$$S^{(1)}(q, \omega) = \sum'_n |(\rho_q^+)_n|^2 \delta(\omega - \omega_{n0}) \quad (2.44)$$

where the prime on the summation denotes the fact that only states which involve two or more quasi particles, of net momentum  $\mathbf{q}$ , are to be considered. It is clear that in the limit of  $\mathbf{q} \rightarrow 0$ ,  $\omega_{n0}(q)$  will not depend sensitively on  $\mathbf{q}$ , and may be expected to approach a constant value. (For example, one adds together quasi-particle states of momenta  $-\mathbf{p}$  and  $\mathbf{p} + \mathbf{q}$ , energies  $\omega_p$  and  $\omega_{p+q}$  to form a pair state of momentum

q. On summing over all possible states  $\mathbf{p}$  and passing to the limit  $\mathbf{q} \rightarrow 0$ , one sees that there is no particular  $\mathbf{q}$  dependence of the resulting set of excitation frequencies.) An estimate of the matrix element  $(\varrho_q^+)_n$  associated with such an excitation may be obtained directly from the  $f$ -sum rule (2.19) which may be written as

$$\sum_n (\varrho_q^+)_n^2 \omega_{n0} = \frac{Nq^2}{2m}. \quad (2.45)$$

In this form it is clear that for the excitations which have a constant energy  $\bar{\omega}$ , say, in the limit  $\mathbf{q} \rightarrow 0$ , the corresponding matrix element must be at least of order  $q$ , or the sum rule (2.45) is violated.

We consider next the matrix element for the current density fluctuation,  $\mathbf{j}_q^+$ , in the limit  $q \rightarrow 0$ . In this limit, one has

$$\lim_{q \rightarrow 0} (\mathbf{j}_q^+)_n = \langle n | \mathbf{J} | 0 \rangle \quad (2.46)$$

where  $\mathbf{J}$  is the total current. Since  $\mathbf{J}$  commutes with the Hamiltonian (for a translationally invariant system), it is good quantum number; therefore, assuming that the limiting procedure is well defined in the limit  $\mathbf{q} \rightarrow 0$ ,  $\langle n | \mathbf{J} | 0 \rangle = 0$ , so that we may write

$$\lim_{q \rightarrow 0} (\mathbf{j}_q^+)_n \sim q^\alpha \quad (\alpha > 0). \quad (2.47)$$

We now make use of longitudinal current conservation, which states that

$$\omega_{n0} (\varrho_q^+)_n = (\mathbf{q} \cdot \mathbf{j}^+)_n$$

according to (2.30). We see that

$$\begin{aligned} \lim_{q \rightarrow 0} \omega_{n0} &= \bar{\omega} \\ \lim_{q \rightarrow 0} (\varrho_q^+)_n &= q^{1+\alpha} \quad (\alpha > 0) \end{aligned} \quad (2.48)$$

for the configurations involving two or more quasi particles. On comparison with (2.45), it follows directly that such configurations can therefore not contribute to the  $f$ -sum rule (2.45). Hence we can write, using (2.43),

$$\lim_{q \rightarrow 0} N Z_q \int_0^\infty d\omega \omega \delta(\omega - \omega_q) = \frac{Nq^2}{2m} \quad (2.49)$$

and hence

$$\lim_{q \rightarrow 0} \omega_q = \frac{q^2}{2mZ_q}. \quad (2.50)$$

Let us now turn to the compressibility sum rule, (2.36), which we write in the form

$$\lim_{q \rightarrow 0} \sum_n \frac{|\langle \rho_q^+ \rangle_{n0}|^2}{\omega_{n0}} = \frac{N}{2ms^2}. \quad (2.51)$$

From (2.46), it follows directly that the configurations involving more than one quasi particle cannot contribute to the compressibility sum rule (2.47). Hence we can write, using (2.43),

$$NZ_q \int_0^\infty d\omega \frac{\delta(\omega - \omega_q)}{\omega_q} = \frac{N}{2ms^2} \quad (2.52)$$

whence we obtain the relation

$$\lim_{q \rightarrow 0} Z_q = \frac{\omega_q}{2ms^2}. \quad (2.53)$$

On combining (2.50) and (2.53) we find

$$\lim_{q \rightarrow 0} \omega_q = sq \quad (2.54)$$

$$\lim_{q \rightarrow 0} Z_q = q/2ms \quad (2.55)$$

whence the result (2.43) follows at once. We furthermore find, on using (2.40), that in the long-wavelength limit the static form factor,  $S_q$ , is given by

$$\lim_{q \rightarrow 0} S_q = \frac{q}{2ms} = Z_q. \quad (2.56)$$

We see therefore that in the long-wavelength limit the single quasi-particle spectrum and the density fluctuation spectrum are identical for liquid helium II; both simply consist of phonons of velocity equal to the macroscopic sound velocity. The phonon contribution exhausts both the  $f$ -sum rule and the compressibility sum rule, and determines the form factor,  $S_q$ . This result is in accord with the experimental mea-

surements of the density fluctuation excitation spectrum by means of inelastic neutron scattering.

## 2. Superfluid Fermion Systems

We next consider the density fluctuation excitation spectrum for a neutral fermion system with attractive interactions. Let us assume the ground state of the system to be a superfluid state, in that the quasi-particle excitations possess an energy gap. This is undoubtedly the situation for fermions with an attractive “s” state interaction; the situation for He<sup>3</sup>, for which the “d” state attractive interaction predominates, is somewhat different and will not be considered here. [See, for example, Morel and Anderson (23).]

The gap in the quasi-particle spectrum serves to rule out any contribution to the dynamic form factor from quasi-particle pairs.

This conclusion follows directly from longitudinal current conservation, since Eq. (2.48) applies to *any* density fluctuation excitation which displays an energy gap in the long-wavelength limit. The multi-pair excitation contribution is likewise negligible. The sole remaining possibility for a long-wavelength density-fluctuation excitation is a longitudinal collective mode corresponding to a coherent pair excitation. We can determine the form of the collective mode spectrum in the long-wavelength limit by requiring that the associated dynamic form factor,

$$S_{\text{coll}}(q, \omega) = NZ_q \delta(\omega - \omega_q) \quad (2.57)$$

satisfy the *f*-sum rule and the compressibility sum rule. We are led at once to the result (2.41). Thus for a superfluid system with an energy gap in the quasi-particle spectrum the dominant long-wavelength excitation likewise consists of phonons of velocity *s*. The difference here is that the phonons represent a collective mode lying within the gap, in contrast to liquid He II, where the phonon mode is identical to the quasi-particle mode in the long-wavelength limit.

## D. RESPONSE FUNCTIONS AT FINITE TEMPERATURES

We consider now the generalization of some of the preceding results to many-particle systems at finite temperatures (24, 25). We first as-

sume that the many-particle system is in equilibrium at some temperature  $T$ . The finite temperature calculation of response functions then differ from those at zero temperature only in that instead of taking the system to be initially in the ground state (in the absence of the perturbation), one describes the system in terms of an average over all possible states  $|m\rangle$ , energy  $E_m$  of the exact Hamiltonian, with a statistical weighting factor  $\exp(-\beta E_m)/\sum_m \exp(-\beta E_m)$  where  $\beta = 1/\kappa T$ . As we proceed, we shall endeavor to indicate both the similarities and the differences between the finite temperature calculations and the  $T = 0$  calculations carried out heretofore.

### 1. Dynamic Form Factor

The dynamic form factor,  $S(q, \omega)$ , is again calculated by considering the probability per unit time that an external particle transfer momentum  $q$  and energy  $\omega$  to the many-particle system. One finds easily

$$S_T(q, \omega) = Z^{-1} \sum_{mn} \exp(-\beta E_m) |(\varrho_q^+)_m|^2 \delta(\omega - \omega_{nm}) \quad (2.58)$$

where

$$Z = \sum_m \exp(-\beta E_m)$$

is the sum over states for the system.  $S(q, \omega)$  is again real; however, it is no longer zero for  $\omega < 0$ , since there is always the possibility that at finite temperatures the system will give up energy to the particle, rather than simply absorbing it. If we interchange indices in (2.58) and, further, assume the system is invariant under time reversal (an assumption we shall make throughout this section), we find that

$$S_T(q, -\omega) = \exp(-\beta\omega) S_T(q, \omega). \quad (2.59)$$

The dynamic form factor is the Fourier transform in space and time of the density-density correlation function,

$$S_T(r, t) = Z^1 \sum_m \exp(-\beta E_m) \langle m | \varrho(r, t)\varrho(0, 0) | m \rangle \quad (2.60)$$

as the reader may readily verify. Thus the physical discussion of the correlation functions, both time dependent and time independent, carried out for  $T = 0$  is obviously valid for finite temperatures.

The derivation of a longitudinal  $f$ -sum rule proceeds in fashion directly analogous to the  $T = 0$  case. At finite temperatures (2.25) is replaced by

$$(Z^{-1}) \sum_m \exp(-\beta E_m) \{ \omega_{nm} |(\varrho_q^+)_m|^2 + \omega_{nm} |(\varrho_q)_{nm}|^2 \} = \frac{Nq^2}{m}. \quad (2.61)$$

If we now make use of time reversal invariance, we may write (2.61) as

$$Z^{-1} \sum_m \exp(-\beta E_m) \omega_{nm} |(\varrho_q^+)_{nm}|^2 = Nq^2/2m. \quad (2.62)$$

On comparing (2.62) with (2.58) and (2.59) we see that the  $f$ -sum rule may likewise be written in either of the following forms:

$$\int_{-\infty}^{\infty} d\omega \omega S_T(q, \omega) = Nq^2/2m \quad (2.63a)$$

$$\int_{-\infty}^{\infty} d\omega \omega S_T(q, \omega) \{1 - \exp(-\beta\omega)\} = Nq^2/m. \quad (2.63b)$$

## 2. Linear Response Functions

Our definition of linear response functions proceeds in fashion identical with that adopted at  $T = 0$ ; the sole difference is that in the defining equation for the density-density response function (2.4), the average  $\langle \varrho(q, \omega) \rangle$  should be calculated by carrying out a suitable average over all possible initial states of the many-particle system. It is left as an exercise for the reader to show that the density-density response function at a temperature  $T$  is given by

$$\chi_T(q, \omega) = Z^{-1} \sum_{mn} \exp(-\beta E_m) \left\{ \frac{|(\varrho_q^+)_{nm}|^2}{\omega - \omega_{nm} + i\eta} - \frac{|(\varrho_q)_{nm}|^2}{\omega + \omega_{nm} + i\eta} \right\} \quad (2.64)$$

which for a state which is invariant under time reversal, may be written as

$$\chi_T(q, \omega) = Z^{-1} \sum_{mn} \exp(-\beta E_m) |(\varrho_q^+)_{nm}|^2 \left\{ \frac{1}{\omega - \omega_{nm} + i\eta} - \frac{1}{\omega + \omega_{nm} + i\eta} \right\}. \quad (2.65)$$

We may write a dispersion relation for  $\chi_T(q, \omega)$  by inspection. Let us define

$$\begin{aligned} \mathcal{L}(q, \omega) = Z^{-1} \sum_{mn} \exp(-\beta E_m) |(\varrho_q^+)_m|^2 & \{ \delta(\omega - \omega_{nm}) \\ & - \delta(\omega + \omega_{nm}) \} \end{aligned} \quad (2.66)$$

It then follows, directly from (2.65), that

$$\chi_T(q, \omega) = \int_{-\infty}^{\infty} d\omega' \frac{\mathcal{L}(q\omega')}{\omega - \omega' + i\eta} \quad (2.67)$$

and, also,

$$\text{Im } \chi_T(q, \omega) = -\pi i \mathcal{L}(q, \omega). \quad (2.68)$$

$\mathcal{L}(q, \omega)$ , which is the dissipative part of the finite temperature density-density response function, plays the role of the spectral density for that function. In that sense it is the finite temperature analog of  $S(q, \omega)$ .

There is a simple relationship between  $\mathcal{L}(q, \omega)$  and  $S_T(q, \omega)$ . If we interchange indices in the second term on the right-hand side of (2.66), we may write

$$\begin{aligned} \mathcal{L}(q, \omega) = Z^{-1} \sum_{mn} \exp(-\beta E_m) & \{ 1 - \exp(-\beta\omega) \} |(\varrho_q^+)_m|^2 \delta(\omega - \omega_{mn}) \\ & = \{ 1 - \exp(-\beta\omega) \} S_T(q, \omega) = S_T(q, \omega) - S_T(q, -\omega). \end{aligned} \quad (2.69)$$

We further note that in terms of the  $\mathcal{L}(q, \omega)$  the longitudinal  $f$ -sum rule (2.63b) takes the simple form

$$\int_{-\infty}^{\infty} d\omega \omega \mathcal{L}(q, \omega) = Nq^2/m \quad (2.70)$$

as soon as one makes use of (2.69). Thus at finite temperatures  $\mathcal{L}(q, \omega)$ , the dissipative part of  $\chi_T(q, \omega)$ , as well as the dynamic form factor obeys a simple sum rule. The sum rule (2.70), could have been derived directly, without reference to  $S_T(q, \omega)$ , if one makes use of (2.64) and (2.61), and the analytic behavior of  $\chi_T(q, \omega)$ .

There is also the compressibility sum rule. One making use of the definition (2.34)

$$\lim_{q \rightarrow 0} \chi_T(q, 0) = -\frac{N}{ms^2}$$

which applies equally well at finite temperatures, we find from (2.67) that

$$\lim_{q \rightarrow 0} \int_{-\infty}^{\infty} d\omega \frac{\mathcal{L}(q, \omega)}{\omega} = \frac{N}{ms^2}. \quad (2.71)$$

### 3. Fluctuation-Dissipation Theorem

At  $T = 0$ , we saw that the dissipative part of the density-density response function,  $\chi(q, \omega)$ , was, aside from a numerical factor, equal to the dynamic form factor,  $S(q, \omega)$ . For a system in thermal equilibrium, there continues to be a simple relation between the linear response of the system and its thermal fluctuations. This relation, known as the fluctuation-dissipation theorem,<sup>7</sup> is essentially contained in (2.69), which furnishes a relation between  $\mathcal{L}(q, \omega)$  and  $S_T(q, \omega)$ . One can state this relation in somewhat more symmetric fashion as follows. Let us define the symmetrized density-density correlation function, according to

$$\tilde{S}_T(r, t) = \frac{\langle \varrho(r, t)\varrho(0, 0) + \varrho(0, 0)\varrho(r, t) \rangle}{2}. \quad (2.72)$$

One finds readily that

$$\tilde{S}_T(q, \omega) = \frac{S_T(q, \omega) + S_T(q, -\omega)}{2}. \quad (2.73)$$

On the other hand,  $\mathcal{L}(q, \omega)$  is the Fourier transform of the commutator

$$\mathcal{L}(r, t) = \langle [\varrho(r, t), \varrho(0, 0)] \rangle \quad (2.74)$$

as the reader may readily verify. The relation between  $\mathcal{L}(q, \omega)$  and  $\tilde{S}_T(q, \omega)$  is readily obtained from (2.69); one finds, on making use of (2.73), that

$$\tilde{S}_T(q, \omega) = \frac{\mathcal{L}(q, \omega)}{2} \coth \frac{\beta\omega}{2}. \quad (2.75)$$

<sup>7</sup> The fluctuation-dissipation theorem was first derived by Nyquist (26) as a relation between the random thermal noise in an electrical circuit and the applied voltage (the latter determining the dissipative part of the circuit behavior). It was later generalized by Callen and Welton (27).

Hence the static form factor may be written as

$$\langle \varrho_q^+ \varrho_q \rangle = NS_q = \int_{-\infty}^{\infty} d\omega \frac{\mathcal{L}(q, \omega)}{2} \coth \frac{\beta\omega}{2} \quad (2.76)$$

which is one of standard forms of the fluctuation-dissipation theorem. To sum up, the commutator of the density fluctuations at two space-time points is related directly to the response of the system and to its dissipative behavior; the anticommutator furnishes a measure of the system fluctuations, and may be determined once the dissipation is known for a system in thermal equilibrium.

#### 4. *Nonequilibrium Systems*

The foregoing results may be generalized without great difficulty to the case of many-particle systems which are not in an equilibrium state. As far as the formal derivation of the expressions for the correlation and response functions is concerned, one need merely redefine the averaging process. Thus, quite generally, one would average over all possible states  $m$  of the exact Hamiltonian, with a statistical weighting factor,  $w_m/\sum_m w_m$ , where  $w_m$  depends on the physical state of the system. In this way one arrives at the appropriate generalized expressions for  $S(q, \omega)$  and  $\chi(q, \omega)$ .

Provided the system is stable, the analytic properties of  $\chi(q, \omega)$  remain unchanged. Using these, and the generalization of the longitudinal current conservation (2.61), one can establish a sum rule for  $\chi(q, \omega)$ . Moreover, the compressibility sum rule goes through in the same way, provided one can *define* a compressibility for the nonequilibrium system. Thus one might attempt to define a “quasi-static” compressibility, in terms of the response to a longitudinal field which varies slowly with time, but still sufficiently rapidly that the system properties are unchanged during the time of measurement.

The essential change for a system which is not in thermal equilibrium is that there no longer exists a simple relation between the system fluctuations and the dissipative part of the response function. An explicit example of such a situation, which has been studied in some detail, is that of electron and ion plasmas which are not at the same temperature. [See, for example, Ichimaru (28).]

### 5. Liquid He II

Let us consider briefly what modifications one might expect in the dynamic form factor of liquid helium at finite temperature. Suppose first we assume that just as at  $T = 0$  the only states of importance in  $S_T(q, \omega)$  are those which correspond to excitation of a single quasi particle from the condensate. In that case, in the long-wavelength limit,  $S_T(q, \omega)$  is unchanged from its zero temperature value, and is given by

$$\lim_{q \rightarrow 0} S_T(q, \omega) = \frac{Nq}{2ms} \delta(\omega - sq). \quad (2.77)$$

Further, on simply integrating over frequencies, one finds the corresponding “zero-temperature” static form factor which is

$$\lim_{q \rightarrow 0} S_T(q) = q/2ms \quad (2.78)$$

The answer, (2.78), is not, in fact, unique; it depends on the relative values of  $q$  and  $T$  that one is considering, as was first shown by Feynman and Cohen (29). To see this, we note that in the limit of  $T$  finite and vanishing  $q$ , we may write:

$$\lim_{q \rightarrow 0} \mathcal{L}(q, \omega) = \lim_{q \rightarrow 0} S_T(q, \omega) \{1 - \exp(-\beta\omega)\} = S_T(q, \omega)\beta\omega \quad (2.79)$$

since under these circumstances,

$$\beta\omega_q \ll 1.$$

On substituting (2.79) into the sum rule, (2.71), one finds a relation between  $S_T(q)$  and the isothermal compressibility,

$$\lim_{q \rightarrow 0} S_T(q) = \frac{1}{\beta ms^2} = \frac{N\kappa}{\beta} \quad (\beta sq \ll 1). \quad (2.80)$$

Closer inspection shows that the linear variation of  $S_T(q)$  begins for values of  $q$  and  $T$  such that

$$\beta sq \gg 1$$

so that (2.78) should be replaced by

$$\lim_{q \rightarrow 0} S_T(q) = \frac{q}{2ms} \quad (\beta sq \gg 1). \quad (2.78a)$$

How is  $S_T(q, \omega)$ , in fact, going to differ from (2.77)? The essential physical difference in the behavior of the system at finite temperatures is the presence of real quasi particles. These can influence matters in two ways. First, the energy of a given quasi particle may depend on the number of quasi particle already present. In that way, the quasi-particle energy will change with temperature; so too will the single quasi-particle contribution to  $\mathcal{L}(q, \omega)$  and  $S_T(q, \omega)$ . Second, there may arise an essentially new sort of contribution to  $\mathcal{L}(q, \omega)$ , one which comes about as a consequence of collisions between the excited quasi particles. At sufficiently low frequencies such collisions may give rise either to first sound, the usual hydrodynamic sound wave, with a velocity equal to the adiabatic sound velocity, or to *second* sound, which corresponds to a temperature wave. The general arguments we have presented above do not permit an estimate of the way in which, at very long wavelengths, the first and second sound poles make their appearance in  $\mathcal{L}(q, \omega)$  — or the strength which such poles will have at a given temperature. Indeed, the determination of such contributions remains one of the interesting, and at present unsolved, problems for a microscopic theory. We further remark that very near the transition temperature, where the number of real excited quasi particles becomes of order  $N$ , all simple arguments of the sort we have presented here will certainly fail.

### III. Correlation and Response: Homogeneous Electron Systems

#### A. DIELECTRIC RESPONSE FUNCTIONS

We consider now the properties of the longitudinal response functions of electron systems. For simplicity we consider only electron plasmas, that is, systems of electrons moving in a uniform background of positive charge. We shall begin with the quantum plasma at  $T = 0$ , and then later discuss the case of finite temperature plasmas. One of our principle aims will be the derivation of exact expressions for the screening length and the plasma oscillation frequency in the limit of very long wavelengths.

### 1. Response to an External Field: $1/\epsilon(q, \omega)$

Let us suppose an external longitudinal electric field,  $\mathcal{D}(r, t)$ , is applied to an electron system. The vector  $\mathcal{D}$  is the “dielectric displacement” defined in elementary electrostatics. It satisfies Poisson’s equation

$$\operatorname{div} \mathcal{D}(r, t) = 4\pi z\varrho_e(r, t), \quad (3.1)$$

where  $z\varrho_e(r, t)$  is the density of “external charge” introduced into the gas at a point  $r$ . The external field will act to polarize the electron system. The induced charge fluctuations may be regarded as producing a space charge field,  $\mathcal{E}_p$ ; the electric field inside the system is thus equal to

$$\mathcal{E}(r, t) = \mathcal{D}(r, t) + \mathcal{E}_p(r, t). \quad (3.2)$$

According to the usual laws of electrostatics,  $\mathcal{E}_p(r, t)$  may be related to the polarization charge density by the equation

$$\operatorname{div} \mathcal{E}_p(r, t) = 4\pi e \langle \varrho(r, t) \rangle. \quad (3.3)$$

When dealing with dielectrics, one must modify (3.3) in order to take into account a surface term, due to the accumulation of charge at the boundary of the sample. Such a term does not enter in the present case, because we assume the system to be closed on itself (for instance, by means of an external “perfectly conducting” wire).

We may combine (3.1)–(3.3) to write

$$\operatorname{div} \mathcal{E}(r, t) = 4\pi \{z\varrho_e(r, t) + e \langle \varrho(r, t) \rangle\} \quad (3.4)$$

as the equation which relates the electric field to the external and induced charge fluctuations. We next take the Fourier transform in space and time of (3.1) and (3.4):

$$i\mathbf{q} \cdot \mathcal{D}(q, \omega) = 4\pi z\varrho_e(q, \omega) \quad (3.5)$$

$$i\mathbf{q} \cdot \mathcal{E}(q, \omega) = 4\pi \{z\varrho_e(q, \omega) + e \langle \varrho(q, \omega) \rangle\}. \quad (3.6)$$

These equations have been obtained with reference to the macroscopic laws of electrostatics; we now extend them to a microscopic level by considering them as applicable for all wave vectors  $q$  and frequency  $\omega$ ,

corresponding to fields which vary arbitrarily rapidly in both space and time. (3.6) thus serves us a definition of the electric field  $\mathcal{E}(q, \omega)$ .

We now make a key assumption: that the dielectric response of the electrons,  $\langle \varrho \rangle$ , is proportional to the applied field  $\mathcal{D}$ . This will be the case if the external field is sufficiently weak; we thus assume that in computing the system response one can neglect coupling terms proportional to  $\mathcal{D}^2$ , etc. It follows at once that  $\mathcal{E}$  will be proportional to  $\mathcal{D}$ . Since both  $\mathcal{D}$  and  $\mathcal{E}$  are purely longitudinal fields, we may write

$$\mathcal{E}(q, \omega) = \frac{\mathcal{D}(q, \omega)}{\varepsilon(q, \omega)}, \quad (3.7)$$

where  $\varepsilon(q, \omega)$  is the frequency and wave vector dependent dielectric constant. We see in (3.7) that  $\varepsilon(q, \omega)$  furnishes a direct measure of the dielectric response of the electron system; it tells us the extent to which the external field,  $\varrho_e$ , is screened by the electronic polarization which it induces.

Thus  $\varepsilon(q, \omega)$  furnishes a natural description of the important screening action of the electron gas. It likewise furnishes a description of the collective modes of the system, the plasmons. The plasmon dispersion relation is simply the condition that one have a nonvanishing charge fluctuation of the electrons in the absence of an external charge. That condition is, according to (3.5) and (3.6),

$$\varepsilon(q, \omega) = 0.$$

If we substitute (3.7) into (3.6), and divide the resulting equation by (3.5), we find:

$$\frac{1}{\varepsilon(q, \omega)} = 1 + \frac{e \langle \varrho(q, \omega) \rangle}{z \varrho_e(q, \omega)} \quad (3.8)$$

on comparing (3.8) with (2.4), and recalling that  $\mathcal{V}_q = 4\pi e^2/q^2$  for the coulomb interaction between the electrons and the external charge density, we see that

$$\frac{1}{\varepsilon(q, \omega)} = 1 + \frac{4\pi e^2}{q^2} \chi(q, \omega). \quad (3.9)$$

The various properties of the dielectric response function then follow

directly from those we have derived earlier for  $\chi(q, \omega)$ . Let us write

$$\varepsilon(q, \omega) = \varepsilon_1(q, \omega) + i\varepsilon_2(q, \omega) \quad (3.10)$$

From (3.9) it is then straightforward to establish the following results for spectral representation

$$\frac{1}{\varepsilon(q, \omega)} = 1 + \frac{4\pi e^2}{q^2} \int_0^\infty d\omega' S(q, \omega') \frac{1}{\omega - \omega' + i\eta} - \frac{1}{\omega + \omega' + i\eta}. \quad (3.11)$$

and for sum rule

$$\int_0^\infty d\omega \omega \frac{\varepsilon_2(q, \omega)}{|\varepsilon(q, \omega)|^2} = \frac{\pi}{2} \omega_p^2 = \frac{2\pi^2 Ne^2}{m} \quad (3.12)$$

where  $\omega_p^2$  is, as before, the square of the electron plasma frequency,  $\omega_p$ .

The response of an electron system to an applied electric field is frequently specified in terms of the conductivity, which is the ratio of the current induced in the system,  $e\langle J \rangle$ , to the effective electric field,  $\mathcal{E}$ . For the present case of fields which vary in space and time, we may write

$$e\langle \mathbf{J}(q, \omega) \rangle = \sigma(q, \omega) \mathcal{E}(q, \omega). \quad (3.13)$$

Here  $e\langle J(q, \omega) \rangle$  is the Fourier transform of the induced current, while  $\sigma(q, \omega)$  is the scalar longitudinal conductivity. We are considering only a longitudinal external field, and have made our customary assumption that the system behavior is isotropic. There is a simple relation between  $\sigma$  and  $\varepsilon$ . To obtain it, we make use of the current conservation equation for the charge and current induced in the electron gas. Thus one has

$$\text{div } \langle \mathbf{J} \rangle + \frac{\partial \langle \varrho \rangle}{\partial t} = 0 \quad (3.14)$$

and

$$q \cdot \langle \mathbf{J} \cdot (\mathbf{q}, \omega) \rangle = \omega \langle \varrho(\mathbf{q}, \omega) \rangle. \quad (3.15)$$

On taking the divergence of (3.13), and making use of Eqs. (3.5–3.7), we find at once

$$\varepsilon(q, \omega) = 1 + \frac{4\pi i \sigma(q, \omega)}{\omega}. \quad (3.16)$$

## 2. Response to a Screened Field: $\chi_s(q, \omega)$

There is another quantity of interest for an electron system, one which we may call a screened response function,  $\chi_s(q, \omega)$ . According to (2.4),  $\chi(q, \omega)$  may be defined (for the case of an external charge in interaction with the electron system), as

$$\chi(q, \omega) = + \frac{\langle \varrho(q, \omega) \rangle}{e\varphi_{\text{ext}}(q, \omega)} \quad (3.17)$$

where  $\varphi_{\text{ext}}(q, \omega)$  is the scalar field potential produced by the external charge. We define  $\chi_s(q, \omega)$  as the response of the system to the scalar potential,  $\varphi(q, \omega)$ , so that

$$\chi_s(q, \omega) = + \frac{\langle \varrho(q, \omega) \rangle}{e\varphi(q, \omega)} . \quad (3.18)$$

We call  $\chi_s(q, \omega)$  the screened response function, because it represents the system response to the screened external probe; according to 3.7  $\varphi(q, \omega) = \varphi e(q, \omega)/\varepsilon(q, \omega)$  so that we can in fact write

$$\chi_s(q, \omega) = \varepsilon(q, \omega) \chi(q, \omega) . \quad (3.19)$$

The utility of  $\chi_s(q, \omega)$  becomes clear if we combine (3.19) with (3.9) to write

$$\varepsilon(q, \omega) = 1 - \frac{4\pi e^2}{q^2} \chi_s(q, \omega) . \quad (3.20)$$

$\chi_s(q, \omega)$  is simply related to the longitudinal conductivity,  $\sigma(q, \omega)$ . On comparing (3.20) and (3.16) we see that

$$\sigma(q, \omega) = \frac{i\omega e^2}{q^2} \chi_s(q, \omega) . \quad (3.21)$$

## 3. Analytic Behavior of $\varepsilon(q, \omega)$

At first sight one would expect that  $\varepsilon(q, \omega)$  is analytic in the upper half-plane, this being the usual property of causal response functions, and more specifically, a property of both  $\chi(q, \omega)$  and  $1/\varepsilon(q, \omega)$ . Closer investigation shows that there does *not* exist a rigorous mathematical demonstration that  $\varepsilon(q, \omega)$  is indeed analytic in the upper half of the

complex  $\omega$  plane. What one can show is that  $\varepsilon(q, \omega)$  will be analytic there, provided (30).

$$\varepsilon(q, 0) > 0. \quad (3.22)$$

One can then make the eminently reasonable physical argument that (3.22) should be valid for an electron system. It is equivalent to the statement that the system cannot overrespond to an external static charge, that is, yield a response which changes the sign of an external static perturbing potential. (Such a phenomenon can, and does take place, for disturbances of finite frequency.) Put another way, if  $\varepsilon(q, 0) > 0$ , one finds that one gains energy on introducing an arbitrarily weak external static charge; again, an unlikely state of affairs.

Assuming, then, that  $\varepsilon(q, \omega)$  is analytic in the upper half of the complex  $\omega$  plane, one can easily write down dispersion relations which connect its real and imaginary parts. One can, moreover, establish a sum rule for  $\varepsilon(q, \omega)$ , one which follows from its asymptotic behavior for large frequencies,

$$\varepsilon(q, \omega) \rightarrow 1 - \omega_p^2/\omega^2 \quad (\omega \rightarrow \infty). \quad (3.23)$$

One finds

$$\int_0^\infty d\omega \omega \varepsilon_2(q, \omega) = \frac{\pi}{2} \omega_p^2 = \frac{2\pi^2 n e^2}{m}. \quad (3.24)$$

## B. THE STATIC DIELECTRIC CONSTANT IN THE LONG-WAVELENGTH LIMIT

We now establish a relation between the compressibility of the electron system and the long-wavelength limit of the static dielectric constant,  $\varepsilon(q, 0)$ . In dealing with an electron plasma it is necessary that one define the compressibility with some care, essentially to allow for the fact that the compressibility is related to the system response to a neutral external disturbance. Hence when we consider a long-wavelength static displacement produced by an external source, we must suppose that the uniform positive charge moves as well, in order to avoid any separation of electric charge. This means that to define the compressibility, we consider the electron response to a test charge plus the appropriate positive charge density, the latter being simply equal to the average induced negative charge density in this limit.

Thus, in place of  $\chi(q, 0)$ , we consider

$$\lim_{q \rightarrow 0} \frac{\langle \varrho(q, 0) \rangle}{4\pi e/q^2 \{Z\varrho_e(q, 0) + e\varrho(q, 0)\}} = \frac{\langle \varrho(q, 0) \rangle}{\left(\frac{4\pi Ze^2}{q^2}\right) \frac{\varrho_e(q, 0)}{\varepsilon(q, 0)}}. \quad (3.25)$$

This response function is simply  $\chi_s(q, 0)$ , whence, without further ado, we can write

$$\lim_{q \rightarrow 0} \chi_s(q, 0) = -\frac{N}{ms^2} \quad (3.26)$$

where  $s$  is, as before, the isothermal sound velocity. If we now make use of (3.20) we obtain our desired result,

$$\lim_{q \rightarrow 0} \varepsilon(q, 0) = 1 + \frac{\omega_p^2}{s^2 q^2}. \quad (3.27)$$

This result was earlier obtained by Nozières (12) and the writer (unpublished), on the basis of the Fermi liquid theory. The present derivation constitutes a proof of the validity of that application of the theory.

We thus see that the screening of a long-length static charge disturbance is an exact property of homogeneous electron system in its ground state, no matter what its density might be. The screening length,

$$\lambda_s = \frac{s}{\omega_p}, \quad (3.28)$$

is simply related to the isothermal sound velocity. We note, too, that the requirement (3.22) is, in the long-wavelength limit, equivalent to the requirement that the system exhibit a positive compressibility. This sort of long-wavelength stability of the electron system is certainly to be expected.

On making use of (3.27) and (3.19), we find

$$\lim_{q \rightarrow 0} \chi(q, 0) = -\frac{q^2}{4\pi e^2}. \quad (3.29)$$

a result which illustrates clearly the difference in the limiting behavior of this quantity for an electron gas and for a neutral system. If we now

make use of the spectral representation for  $\chi(q, 0)$ , we find that for an electron system, the “compressibility” sum rule takes the form

$$\lim_{q \rightarrow 0} \int_0^\infty d\omega \frac{S(q, \omega)}{\omega} = \frac{q^2}{8\pi_e^2}. \quad (3.30)$$

Another long-wavelength sum rule may be derived from (3.27). One of the Kramers-Kronig relations which relates  $\varepsilon_1$ , and  $\varepsilon_2$  may be written as

$$\varepsilon_1(q, \omega) = 1 + \frac{2}{\pi} \int_0^\infty d\omega' \left\{ \varepsilon_2(q, \omega') \frac{\omega'}{\omega^2 - \omega'^2} \right\}. \quad (3.31)$$

On comparing (3.31) and (3.27), we find

$$\lim_{q \rightarrow 0} \int_0^\infty d\omega \frac{\varepsilon_2(q, \omega)}{\omega} = \frac{\pi}{2} \frac{\omega_p^2}{s^2 q^2}. \quad (3.32)$$

### C. FINITE TEMPERATURE ELECTRON RESPONSE FUNCTIONS

The dielectric response function, and the related correlation functions for electron systems at finite temperatures, are easily obtained with the aid of the results we have established for density-density response function at finite temperatures. We quote here the finite temperature analogs of the results obtained earlier for the ground state.

#### 1. Dielectric Response Function

$$\frac{1}{\varepsilon_T(q, \omega)} = 1 + \frac{4\pi e^2}{q^2} \chi_T(q, \omega) \quad (3.33)$$

#### 2. Spectral Representation

$$\frac{1}{\varepsilon_T(q, \omega)} = 1 + \frac{4e^2}{q^2} \int_{-\infty}^\infty d\omega' \frac{\mathcal{L}(q, \omega')}{\omega - \omega' + i\delta}. \quad (3.34)$$

#### 3. Sum Rules

$$i \int_{-\infty}^\infty d\omega \left\{ \text{Im} \frac{1}{\varepsilon_T(q, \omega)} \right\} \omega = \pi \omega_p^2 \quad (3.35)$$

$$\lim_{q \rightarrow 0} i \int_{-\infty}^{\infty} d\omega \left\{ \text{Im} \frac{1}{\varepsilon_T(q, \omega)} \right\} \frac{1}{\omega} = \frac{\pi}{2} \quad (3.36)$$

$$- i \int_{-\infty}^{\infty} d\omega \omega \text{ Im } \varepsilon_T(q, \omega) = \pi \omega_p^2 \quad (3.37)$$

$$\lim_{q \rightarrow 0} - i \int_{-\infty}^{\infty} \frac{d\omega}{\omega} \text{ Im } \varepsilon_T(q, \omega) = \frac{\pi \omega_p^2}{s^2 q^2}. \quad (3.38)$$

#### 4. Static Dielectric Constant

$$\lim_{q \rightarrow 0} \varepsilon_T(q, 0) = 1 + \frac{\omega_p^2}{s^2 q^2} \quad (3.39)$$

where  $s$  is the isothermal sound velocity.

### D. SCREENING AND PLASMA OSCILLATION IN ELECTRON SYSTEMS

#### 1. Quantum and Classical Plasmas

It is evident from (3.27) and (3.39) that the screening of a low frequency charge disturbance is an exact property of both quantum and classical plasmas. The characteristic screening length for both systems is

$$\lambda_s = \frac{s}{\omega_p}$$

where  $s$ , the isothermal sound velocity, is of the order of magnitude of the root mean square electron velocity.

The backflow about a slowly moving charged impurity is likewise an exact property of the plasma. We remark that the density fluctuation induced by an impurity of velocity  $\mathbf{V}_e$  is

$$\langle \rho(q, \mathbf{q} \cdot \mathbf{V}_e) \rangle = \frac{4\pi e^2}{q^2} \chi(q, \mathbf{q} \cdot \mathbf{V}_e) \quad (3.40)$$

since the impurity behaves like a test charge of frequency  $\omega = \mathbf{q} \cdot \mathbf{V}_e$ . With the aid of longitudinal current conservation, we may write

$$\langle \mathbf{q} \cdot \mathbf{j}(q, \mathbf{q} \cdot \mathbf{V}_e) \rangle = (\mathbf{q} \cdot \mathbf{V}_e) \frac{4\pi e^2}{q^2} \chi(q, \mathbf{q} \cdot \mathbf{V}_e) \cong (\mathbf{q} \cdot \mathbf{V}_e) \frac{4\pi e^2}{q^2} \chi(q, 0) \quad (3.41)$$

for the induced current fluctuation. Upon making use of (3.29), we find

$$\langle \mathbf{q} \cdot \mathbf{j}(q, \mathbf{q} \cdot \mathbf{V}_e) \rangle = -\mathbf{q} \cdot \mathbf{V}_e \quad (3.42)$$

from which it follows that the total current, particle plus its associated screening cloud, is divergence free. We have made no distinction in this derivation between the quantum and the classical plasma; it is valid at any temperature and density.

Because both  $\varepsilon(q, \omega)$  and  $\varepsilon^{-1}(q, \omega)$  satisfy sum rules, there exist four separate sum rules for the spectral density,  $\mathcal{L}(q, \omega)$ , of a finite temperature plasma [and for the dynamic form factor,  $S(q, \omega)$ , for a quantum plasma in its ground state]. We may write these in the following way:

$$\int_{-\infty}^{\infty} d\omega \omega \mathcal{L}(q, \omega) = \frac{Nq^2}{m} = 2 \int_0^{\infty} d\omega \omega S(q, \omega) \quad (3.43)$$

$$\lim_{q \rightarrow 0} \int_{-\infty}^{\infty} d\omega \frac{\mathcal{L}(q, \omega)}{\omega} = \frac{q^2}{4\pi e^2} = 2 \lim_{q \rightarrow 0} \int_0^{\infty} d\omega \frac{S(q, \omega)}{\omega} \quad (3.44)$$

$$\begin{aligned} \int_{-\infty}^{\infty} d\omega \omega \mathcal{L}(q, \omega) |\varepsilon(q, \omega)|^2 &= \frac{Nq^2}{m} \\ &= 2 \int_0^{\infty} d\omega \omega S(q, \omega) |\varepsilon(q, \omega)|^2 \end{aligned} \quad (3.45)$$

$$\begin{aligned} \lim_{q \rightarrow 0} \int_{-\infty}^{\infty} d\omega \frac{\mathcal{L}(q, \omega)}{\omega} |\varepsilon(q, \omega)|^2 &= \frac{N}{ms^2} \\ &= 2 \lim_{q \rightarrow 0} \int_0^{\infty} \frac{d\omega}{\omega} S(q, \omega) |\varepsilon(q, \omega)|^2. \end{aligned} \quad (3.46)$$

In the long-wavelength limit, the first two sum rules are exhausted by the plasma oscillations; the latter two sum rules measure the single-particle contribution to the spectral density, and are unaffected by the plasma oscillations.

To see how this comes about, let us write

$$\mathcal{L}(q, \omega) = \mathcal{L}_p(q, \omega) + \mathcal{L}^{(1)}(q, \omega) \quad (3.47)$$

where  $\mathcal{L}_p(q, \omega)$  represents the spectral density for the plasmon modes. It is then straightforward to show that if

$$\lim_{q \rightarrow 0} \mathcal{L}_p(q, \omega) = \frac{q^2 N}{2m\omega_p} \{ \delta(\omega - \omega_p) - \delta(\omega + \omega_p) \} \quad (3.48)$$

then  $\mathcal{L}_p(q, \omega)$  satisfies *both* sum rules, (3.43) and (3.44). It follows that plasma oscillations at a frequency  $\omega_p$  are the dominant long-wavelength excitation mode of homogeneous plasmas, no matter what their temperature and density.

It is also clear that the plasmons do not contribute at all to the sum rules (3.45) and (3.46), since

$$\lim_{q \rightarrow 0} \varepsilon(q, \omega_p) = 0. \quad (3.49)$$

This result is scarcely surprising, since these two sum rules are sum rules on  $\varepsilon_2$ , where only single-particle excitations play a role.

Let us study the pair excitation part of  $S(q, \omega)$  in further detail. We consider first the contribution to the sum rules from single quasi-particle, quasi-hole pairs in the limit  $q \rightarrow 0$ . As we have remarked earlier in this limit, a typical pair excitation frequency is  $q\nu_F$ . For the free-particle system, the long-wavelength matrix element,  $(\varrho_q^+)_n$ , is of order 1 for the states which contribute; the number of such states is of order  $q/p_F$ . In the interacting electron gas, one has, rather,

$$\lim_{q \rightarrow 0} (\varrho_q^+)_n \sim (q/p_F)^2 \quad (\text{pair states}), \quad (3.50)$$

as a result of the screening of the single-particle-like transitions. That this must be the case is clear from, for example, Eq. (3.45), which we write as

$$\sum_n |(\varrho_q^+)_n|^2 \omega_{n0} |\varepsilon(q, \omega_{n0})|^2 = Nq^2/2m. \quad (3.51)$$

For the essentially low frequency transitions which enter here, one has

$$|\varepsilon(q, \omega_{n0})|^2 \sim p_F^{-4}/q^4$$

as a manifestation of dynamic screening. With  $(\varrho_q^+) \sim q^2$ ,  $\omega_{n0} \sim q$ , and the number of states which contribute  $q$ , one gets a single pair contribution to (3.51) and, likewise to (3.46).

The contribution from multipair states (containing at least two quasi

particles and quasi-holes) may be estimated in the following way. In the limit  $q \rightarrow 0$ , the average multipair excitation frequency is a constant,  $\omega$ . Consideration of longitudinal current conservation

$$\omega_{n0}(\varrho_q^+)_n = (\mathbf{q} \cdot \mathbf{j}_q^+)_n$$

yields a matrix element,  $(\varrho_q^+)_n \sim q^2$ , since  $(j_q^+)_n$  must be of order  $q$  in the long-wavelength limit. Finally, there are no particularly preferred excitation frequencies for the multipair states. If one takes maximum advantage of  $|\epsilon(q, \omega)|^2$  by concentrating on the low energy contributions to, say, (3.51), one must restrict the summation to a frequency region  $\sim qv_F$ . As a result one finds a multipair contribution which is at least of order  $q^5$ , for both sum rules. We conclude that quasi-particle, quasi-hole pair excitations exhaust both sum rules.

There are several interesting by-products of this rather lengthy discussion. One is the fact that plasmon damping is negligible in the long-wavelength limit. For a quantum plasma in its ground state, plasmon damping arises from a coupling of a plasma oscillation to a multipair configuration. Since such configurations do not effect  $S(q, \omega)$  to lowest order in  $q$ , plasmons are correspondingly undamped to this order. In fact, we may use the above arguments to show that the plasmon lifetime,  $\tau$ , against decay into a multipair configuration, is of order  $1/q^2$ . To see this, remark that the multipair contribution to the sum rule, (3.43), is of order  $q^4$ , a result which is comparable with that coming from the  $q^2$  term in the plasmon dispersion relation. Hence an overlap of the plasmon spectrum with multipair excitations in this order is not inconsistent with the sum rule, and may be expected to occur.

We remark also that the backflow which surrounds a slowly moving charged impurity in a plasma may be regarded as consisting in a virtual cloud of plasmons. As we have seen above, the backflow is determined by  $\chi(q, 0)$ . This latter quantity is, according to the sum rule (3.44), determined entirely by the plasmon modes. It follows that the backflow is equivalent to an induced "plasmon" current, since only plasmons need be involved to determine the entire effect.<sup>8</sup> This result is equally valid for the classical plasma.

<sup>8</sup> Such a result was obtained some time ago by Pines and Schieffer (31), who described the backflow with the aid of the Bohm-Pines collective description of plasmon behavior.

## 2. Superconductors

We are now in a position to discuss the dynamic form factor for a superconductor. For simplicity, we consider the superconductor to be in its ground state. We again make use of the sum rules (3.43) and (3.44). We consider first the pair excitation contribution to these sum rules in the long-wavelength limit. Such pair excitations possess a constant energy,  $2\Delta$ . Their matrix element,  $(\varrho_q^+)_n$ , is of order  $q^{1+\alpha}$  ( $\alpha > 0$ ), according to our arguments based on the long-wavelength limit of the current conservation condition. It follows that the excitations do not contribute to the sum rules. The same argument applies to the multi-pair excitations. As a result, one finds for the superconductor a result identical to that obtained above for the quantum plasma:

$$\lim_{q \rightarrow 0} S(q, \omega) = \frac{q^2 N}{2m\omega_p} (\omega - \omega_p)$$

The dominant long-wavelength excitations are plasmons of frequency  $\omega_p$ ; to lowest order in  $q$  the long-wavelength plasmons are unaffected by the transition from the normal to the superconducting state.

We next remark that our derivation of the long-wavelength static dielectric constant was in no way dependent on whether the ground state of the electron system represented a normal state or a superconducting state of the electron gas. We conclude that, at least in this limit, the screening action of the superconductor is changed from that of the normal electron system only to the extent that the compressibility is changed — the latter change being quite negligible (of order 1 part in  $10^5$ ).

We have thus shown that static long-wavelength screening and the long-wavelength plasma oscillations are essentially unaffected in the transition from the normal to the superconducting state.

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# The Electron-Phonon Interaction in Normal and Superconducting Metals<sup>1</sup>

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## I. Correlation Function Approach

This series of lectures has two purposes:

- (a) To report on recent developments in the theory of the electron-phonon interaction in metals.
- (b) To serve as an introduction to the use of Green's function methods in many particle physics.<sup>2</sup>

We begin by noticing that one of the very simplest things you can do to a many-particle system is add a particle to it or pull one out. For this reason, it is very convenient to describe the properties of the system in terms of the creation and annihilation operators:

$C_p^+(t')$  = creation operator

$C_p(t)$  = annihilation operator.

When these operators act to the right on a state of the system, they respectively add a particle with momentum  $p$  to this state at the time  $t'$  and pull one out at the time  $t$ .

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<sup>2</sup> The Green's function methods that I shall employ can be traced back to the work of Martin and Schwinger (1). These methods are discussed in detail in a book by Baym and Kadanoff (2).

We shall also make use of the wave field operators  $\psi^+(r', t')$  and  $\psi(r, t)$  which respectively add and subtract a particle at the space-time points  $r', t'$  and  $r, t$ . If one quantizes in a box of unit volume with periodic boundary conditions the two sets of operators are related by

$$\begin{aligned}\psi^+(r', t') &= \sum_p \exp(-ip \cdot r') C_p^+(t') \\ \psi(r, t) &= \sum_p \exp(ip \cdot r) C_p(t)\end{aligned}\quad (1.1)$$

where the momentum sums run over all the allowed momenta in the box. (We use units in which  $\hbar = 1$ .)

These are all Heisenberg representation operators and, as such, they have the time dependence

$$A(t) = \exp(iH't) \quad A(0) = \exp(-iH't) \quad (1.2)$$

Of course, we may choose the zero point of energy at our convenience. We choose our zero point by using in (1.2)

$$H' = H - \mu N \quad (1.3)$$

where  $H$  is the standard Hamiltonian,  $\mu$  the chemical potential, and  $N$  the number operator to be the basic operator which gives the time dependence of our operators.

The two basic correlation functions which we shall discuss are

$$\begin{aligned}G^>(r, t; r', t') &= \langle \psi(r, t) \psi^+(r', t') \rangle \\ G^<(r, t; r', t') &= \langle \psi^+(r', t') \psi(r, t) \rangle\end{aligned}\quad (1.4)$$

where  $\langle \rangle$  stands for both a quantum-mechanical average and a statistical average according to the averaging procedure defined by the grand canonical ensemble of statistical mechanics.

Because of the equilibrium nature of the system all physical quantities are independent of the time. Furthermore, our periodic boundary condition in space guarantees the spatial homogeneity of the system. Therefore,  $G^>$  and  $G^<$  cannot depend upon  $r$  and  $r'$  or  $t$  and  $t'$  individually but only upon the difference variables  $r - r'$ ,  $t - t'$ . This fact

is conveniently included by using the Fourier representations of these quantities as

$$\begin{aligned} G^> (r, t; r', t') &= G^> (r - r'; t - t') \\ &= \sum_p \int \frac{d\omega}{2\pi} \exp [ip \cdot (r - r') - i\omega(t - t')] G^> (p, \omega) \\ &= \sum_p \exp [ip \cdot (r - r')] \langle C_p(t) C_p^+(t') \rangle \end{aligned} \quad (1.5a)$$

while

$$\begin{aligned} G^< (r - r'; t - t') &= \sum_p \exp [ip \cdot (r - r')] \langle C_p^+(t') C_p(t) \rangle \\ \sum_p &= \int \frac{d\omega}{2\pi} \exp [ip \cdot (r - r') - i\omega(t - t')] G^< (p, \omega). \end{aligned} \quad (1.5b)$$

$G^> (p, \omega)$  and  $G^< (p, \omega)$  have a very direct physical interpretation. Consider  $G^< (p, \omega)$ . We know that  $C_p(t)$  is an operator which removes a particle with momentum at the time  $t$ . In the usual quantum-mechanical way, the time Fourier transform of  $C_p(t)$  removes a particle of momentum  $p$  and energy  $\omega$ . But, if you are going to remove such a particle, there must be a particle with this energy and momentum present initially. For this reason,

$$G^< (p, \omega) = \text{density of particles with momentum } p \text{ and energy } \omega. \quad (1.6)$$

Because the time Fourier transform of  $C_p^+(t')$  adds a particle with momentum  $p$  and energy  $\omega$ , we can see that  $G^> (p, \omega)$  measures the system's ability to accept a particle with this energy and momentum. That is,

$$G^> (p, \omega) = \text{effective density of states in } p, \omega \quad (1.7)$$

or, if you prefer, this may be termed a density of holes.

These statements (1.6) and (1.7) will be very important for our future discussions. Therefore, we examine them in a little detail. From (1.5b), the total number of particles with momentum  $p$ ,  $N_p = C_p^+ C_p$ , is given by

$$\langle N_p \rangle = \langle C_p^+ C_p \rangle = \int \frac{d\omega}{2\pi} G^< (p, \omega) \quad (1.8)$$

which is the integral over all energies of the density as function of energy. Also the total effective density of states is, from (1.5b)

$$\int \frac{d\omega}{2\pi} G^> (p, \omega) = \langle C_p C_p^+ \rangle.$$

However, the creation and annihilation operators satisfy the equal time commutation or anticommutation relation

$$C_p(t) C_p^+(t) \mp C_p^+(t) C_p(t) = 1 \quad (1.9)$$

where the upper sign here, and in what follows, is appropriate when the particle obey Bose statistics and the lower sign is for Fermi statistics. Therefore, the total density of states is

$$\int \frac{d\omega}{2\pi} G^> (p, \omega) = 1 \pm \langle N_p \rangle. \quad (1.10)$$

For fermions as  $\langle N_p \rangle$  increases, the effective density of states decreases while for bosons, which are very gregarious, the larger the occupation of a state, the larger is the effective density of states.

To illustrate the meaning of  $G^>$  and  $G^<$ , let us consider a tunneling experiment. In its simplest form this is an experiment in which two

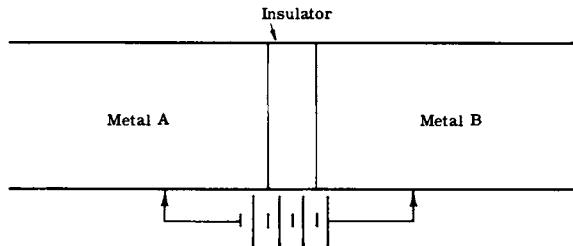


FIG. 1

conductors are separated by a thin insulating layer and a DC voltage is applied across the gap. The induced current can then be measured as a function of voltage.

Electrons cross the gap via a quantum-mechanical tunneling process. Following many recent authors (3; 4) (see the chapter by R. Prange in

this volume) we can describe the tunneling by a tunneling amplitude  $T(p', p)$ , which is the probability amplitude for an electron with momentum  $p$  on one side of the gap reappearing with momentum  $p'$  on the other. (This is essentially the overlap between the wave functions on opposite sides of the insulator.)

We calculate the tunneling rate from A to B by making use of the golden rule, which states that a transition rate is proportional to a matrix element squared [here,  $|T(p, p')|^2$ ], an energy conserving  $\delta$ -function, a density of initial and final states, summed over all initial and all final states. Thus,

$$\frac{dN}{dt} \Big|_{A \rightarrow B} = \sum_{pp'} \int \frac{d\omega}{2\pi} \int \frac{d\omega'}{2\pi} |T(p, p')|^2 \\ 2\pi\delta(\omega - \omega' + eV) G_A^<(p, \omega) G_B^>(p', \omega'). \quad (1.11a)$$

Here the  $\delta$ -function requires that the energy change on traversing the barrier be  $eV$ .  $G_A^<$  and  $G_B^>$ , of course, represent the density of particles in A and the density of states in B.

The rate of tunneling in the opposite sense is given by a result identical to (1.11a) except for the appearance of the density of particles in B and the density of states in A, that is

$$\frac{dN}{dt} \Big|_{B \rightarrow A} = \sum_{pp'} \int \frac{d\omega}{2\pi} \int \frac{d\omega'}{2\pi} |T(p, p')|^2 \\ 2\pi\delta(\omega - \omega' + eV) G_A^>(p, \omega) G_B^<(p', \omega'). \quad (1.11b)$$

To obtain the net tunneling rate we subtract (1.11b) from (1.11a) to find

$$\text{net } \frac{dN}{dt} = \sum_{pp'} \int \frac{d\omega}{2\pi} \int \frac{d\omega'}{2\pi} |T(p, p')|^2 2\pi\delta(\omega - \omega' + eV) \\ [G_A^<(p, \omega) G_B^>(p', \omega') - G_A^>(p, \omega) G_B^<(p', \omega')]. \quad (1.12)$$

Equation (1.12) may be used to predict the tunneling rate in all cases except that in which both conductors are in a superconducting state. In that case, some very exceptional behavior results as first predicted by Josephson (5) and experimentally verified by Anderson and Rowell (6).

This kind of tunneling is discussed in detail by P. W. Anderson in this volume.

In all but this exceptional case, one expects that, as  $V \rightarrow 0$ , the tunneling current should vanish. However, if A and B are different materials so that  $G_A^< \neq G_B^<$ , Eq. (1.12) does not appear to predict the vanishing of the current at  $V \rightarrow 0$ .

In order to see how this vanishing does in fact occur, we must make use of a kind of detailed balancing condition which relates the density of particles and the density of states. It is a characteristic feature of a system in equilibrium at temperature  $T$  that the relative occupation of a state with energy  $\omega$  is proportional to  $\exp(-\beta\omega)$ , where  $\beta = (kT)^{-1}$ , and  $k$  is the Boltzmann constant. This characteristic feature shows up as a restriction upon  $G^<$  and  $G^>$  that, for a system in equilibrium,

$$G^<(p, \omega) = \exp(-\beta\omega) G^>(p, \omega) \quad (1.13)$$

$$(\text{density of particles}) = \exp(-\beta\omega) (\text{density of states}).$$

We shall prove this condition in a moment. For now let us see its consequences in the tunneling rate given by (1.12). We use (1.13) to eliminate  $G_A^<$  in favor of  $G_A^>$  and  $G_B^<$  in favor of  $G_B^>$ . Then (1.12) becomes

$$\begin{aligned} \text{net } \frac{dN}{dt} &= \sum \int \int |T|^2 2\pi\delta(\omega - \omega' + eV) \\ &\quad G_A^>(p, \omega) G_B^>(p', \omega') [\exp(-\beta\omega) - \exp(-\beta\omega')]. \end{aligned}$$

Clearly now as  $V \rightarrow 0$ , so does the current.

Equation (1.13) will be quite crucial for us so we consider its proof in some detail. In the ground canonical ensemble, the expectation value of any operator is given by

$$\begin{aligned} \langle X \rangle &= \sum_{\xi} \exp[-\beta(E_{\xi} - \mu N_{\xi})] \langle \xi | X | \xi \rangle / Z_G \\ &= \text{Tr} [\exp(-\beta H') X] / Z_G \end{aligned} \quad (1.14)$$

where the sum runs over all possible states with any number of particles and where

$$Z_G = \sum_{\xi} \exp[-\beta(E_{\xi} - \mu N_{\xi})] = \text{Tr} [\exp(-\beta H')]$$

is the grand partition function.

Now consider the two functions

$$\begin{aligned} F^>(t) &= \langle A(t) X \rangle \\ F^<(t) &= \langle X A(t) \rangle. \end{aligned} \quad (1.15)$$

If  $A(t)$  is a Heisenberg representation operator with no explicit time dependence

$$A(t) = \exp(iH't) \quad A(0) = \exp(-iH't). \quad (1.2)$$

Equation (1.2) can be used to define  $A(t)$  for complex values of the time. Now consider, in particular,

$$\begin{aligned} F^>(t) |_{t=-i\beta} &= \langle \exp(+\beta H') A(0) \exp(-\beta H') X \rangle \\ &= \text{Tr} [\exp(-\beta H') \exp(\beta H') A(0) \exp(-\beta H') X] / Z_G \\ &= \text{Tr} [A(0) \exp(-\beta H') X] / Z_G \\ &= \text{Tr} [\exp(-\beta H') X A(0)] / Z_G = \langle X A(0) \rangle. \end{aligned}$$

Consequently,

$$F^>(t) |_{t=-i\beta} = F^<(t) |_{t=0}. \quad (1.16)$$

Let us apply this theorem to  $G^>$  and  $G^<$ . Equation (1.16) implies that

$$\begin{aligned} G^>(r, t; r', t') |_{t=-i\beta} &= G^<(r, t; r', t') |_{t=0} \\ &\int \frac{d\omega}{2\pi} \exp[-i\omega(t-t')] G^>(p, \omega) |_{t=-i\beta} \\ &= \int \frac{d\omega}{2\pi} \exp[-i\omega(t-t')] G^<(p, \omega) |_{t=0} \end{aligned} \quad (1.17)$$

or

$$\int \frac{d\omega}{2\pi} \exp(i\omega t') \exp(-\beta\omega) G^>(p, \omega) = \int \frac{d\omega}{2\pi} \exp(i\omega t') G^<(p, \omega),$$

which immediately leads us back to (1.13).

The functions  $G^>(p, \omega)$  and  $G^<(p, \omega)$  contain a tremendous amount of useful information. They describe, as we have seen, the density of

particles and the density of states, and they describe all the thermodynamic properties of the system. Consequently, it is quite worthwhile to know these functions.

In actual calculations, it is very convenient to make use of the spectral weight function

$$\begin{aligned} A(p, \omega) &= G^>(p, \omega) \mp G^<(p, \omega) \\ &= \text{Fourier transform } \langle C_p(t)C_p^+(t') \mp C_p^+(t')C_p(t) \rangle. \end{aligned} \quad (1.18)$$

The usefulness of  $A(p, \omega)$  is derived from the equal time commutation relation (1.7), which implies the sum rule

$$\int \frac{d\omega}{2\pi} A(p, \omega) = 1. \quad (1.19)$$

By making use of the detailed balancing condition (1.13) together with the definition (1.17) we can express  $G^>$  and  $G^<$  in terms of  $A$  as

$$\begin{aligned} G^>(p, \omega) &= [1 \pm f(\omega)] A(p, \omega) \\ G^<(p, \omega) &= f(\omega) A(p, \omega) \end{aligned} \quad (1.20)$$

where

$$f(\omega) = \frac{1}{\exp(\beta\omega) \mp 1} \quad (1.21)$$

is the a priori probability of observing a particle with energy  $\omega$  in the grand canonical ensemble.

Now we must face the hard job of determining  $G^>$  and  $G^<$ . To see how this goes consider just the trivial case of free particles. In general,  $\omega$  represents the total energy of a particle added to the system, its kinetic energy plus the interaction energy that it aims through its interaction with all the other particles in the system. However, for noninteracting particles  $\omega$  must be just the kinetic energy

$$\varepsilon_p = p^2/2m - \mu. \quad (1.22)$$

Therefore  $G^>$ ,  $G^<$ , and  $A$  are all proportional to  $\delta(\omega - \varepsilon_p)$ . However, for  $A(p, \omega)$ , we have a sum rule (1.18) which tells us the constant of proportionality, so that

$$A(p, \omega) = 2\pi\delta(\omega - \varepsilon_p). \quad (1.23)$$

Using (1.22), we can easily calculate the density of particles with momentum  $p$  as

$$\begin{aligned}\langle N_p \rangle &= \int \frac{d\omega}{2\pi} G^<(p, \omega) = \int \frac{d\omega}{2\pi} f(\omega) A(p, \omega) \\ &= f(\varepsilon_p) \\ &= \frac{1}{\exp [\beta(p^2/2m - \mu)] \mp 1},\end{aligned}$$

the familiar result for a system of noninteracting fermions or bosons.

In generalizing these free particle results, it is convenient for us to define a function of a complex variable  $z$ :

$$G(p, z) = \int \frac{d\omega}{2\pi} \frac{A(p, \omega)}{z - \omega}. \quad (1.24)$$

For the free-particle system:

$$G(p, z) = \frac{1}{z - \varepsilon_p}. \quad (1.25)$$

In the general case,

$$G(p, z) = \frac{1}{z - \varepsilon_p - \Sigma(p, z)}. \quad (1.26)$$

Since the variable  $\omega$  represents the total energy of an added particle we can interpret  $\Sigma(p, \omega)$  [that is,  $\Sigma(p, z)$  for real  $z$ ] as the extra interaction energy that would be produced by the addition of a hypothetical particle of momentum  $p$  and energy  $\omega$ . For this reason  $\Sigma$  is termed the self-energy. If the hypothetical energy is to be a realizable energy difference  $\omega$  must satisfy the dispersion relation

$$\omega = \varepsilon_p + \Sigma(p, \omega). \quad (1.27)$$

Notice that these energy levels give the position of the poles of  $G(p, z)$  and hence of  $\delta$ -function singularities in  $A(p, \omega)$ .

To illustrate how  $\Sigma(p, \omega)$  may be calculated, let us consider the interaction of electrons with longitudinal phonons. In the simplest model,

this interaction may be represented by the interaction Hamiltonian

$$H_{ep} = \sum_q [v_q a_q \int dr \exp(iq \cdot r) \psi^+(r) \psi(r) + v_q^* a_q^+ \int dr \exp(-iq \cdot r) \psi^+(r) \psi(r)]. \quad (1.28)$$

Here  $a_q^+$  and  $a_q$  are phonon creation and annihilation operators, and  $v_q$  is a matrix element which measures the coupling strength. We can rewrite (1.27) as

$$H_{ep} = \sum_{qp} (v_q a_q C_{p+q}^+ C_p + v_q^* a_q^+ C_{p,q}^+ C_p) \quad (1.29)$$

The first term in (1.29) describes a process in which an electron with momentum  $p$  absorbs a phonon with momentum  $q$  and hence scatters into the momentum state  $p + q$ . The second term describes a similar process in which a phonon is emitted.

As a preliminary to the calculation of  $\Sigma(p, \omega)$ , we calculate  $\langle H_{ep} \rangle$  in second order perturbation theory. As usual, the second order perturbation theory gives a sum over all initial and the final states of a matrix element squared divided by an energy denominator which is the difference in energy between the initial and the final state. In this case

$$\begin{aligned} \langle H_{ep} \rangle &= \int \frac{d\omega}{2\pi} \int \frac{d\omega}{2\pi} \sum_{p,p'} G^<(p, \omega) G^>(p', \omega') |v_q|^2 \\ &\quad \left[ \frac{N_q}{\omega + \omega_q - \omega'} + \frac{N_q + 1}{\omega - \omega_q - \omega'} \right]_{q=|p-p'|}. \end{aligned} \quad (1.30)$$

Here  $\omega_q$  is the energy of a phonon with wave vector  $q$ , and

$$N_q = \frac{1}{\exp(\beta\omega_q) - 1}$$

is the equilibrium number of phonons with wave vector  $q$ . The first term in the square bracket of (1.30) describes a process in which an electron with  $(p, \omega)$  absorbs a phonon and scatters into the state  $(p', \omega')$ . The energy difference between the initial state and the final state is  $\omega + \omega_q - \omega'$ . The density of initial states is given by the density of

electrons,  $G^<(p, \omega)$  times the density of phonons,  $N_q$ , and the density of final states if  $G^>(p', \omega')$ . In just the same way, the other term in the square bracket gives the energy shift due to phonon emission processes.

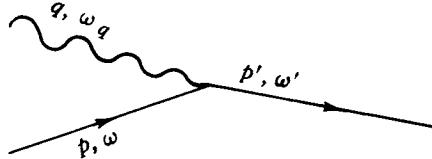


FIG. 2

We calculate the self-energy as the change in the interaction energy which occurs upon the addition to the system of a particle with momentum  $p$  and energy  $\omega$ . This addition may be represented by changing the density of particles according to

$$G^<(p', \omega') \rightarrow G^<(p', \omega') + 2\pi\delta(\omega - \omega') \delta_{p,p'}. \quad (1.31a)$$

The added particle also changes the density of states. Since an electron is a fermion, the change is a reduction in the density of states according to

$$G^>(p', \omega') \rightarrow G^>(p', \omega') - 2\pi\delta(\omega - \omega') \delta_{p,p'}. \quad (1.31b)$$

The self-energy is then defined as

$$\Sigma(p, \omega) = \delta\langle H_{ep} \rangle \quad (1.32)$$

$$\begin{aligned} &= \int \frac{d\omega'}{2\pi} \sum_{p'} |v_q|^2 \left\{ G^>(p', \omega') \left[ \frac{N_q}{\omega + \omega_q - \omega'} + \frac{N_q + 1}{\omega - \omega_q - \omega'} \right] \right. \\ &\quad \left. + G^<(p', \omega') \left[ \frac{N_q}{\omega - \omega_q - \omega'} + \frac{N_q + 1}{\omega + \omega_q - \omega'} \right] \right\}_{q=|p-p'|}. \end{aligned}$$

This result can again be understood in terms of second order perturbation theory.<sup>3</sup>

<sup>3</sup> The argument given here may be extended, but only with considerable care, to obtain  $\Sigma$  as a variational derivative of an object related to  $\langle H_{ep} \rangle$  with respect to  $G$ . A rigorous version of this argument is presented by Baym (7).

Before we go any further, we must face a serious difficulty.  $\Sigma(p, \omega)$  is, strictly speaking, undefined at a fantastic number of different points on the real axis: all those points at which the energy denominator may vanish. The exact position of these singularities depends in great detail upon the exact size and shape of the system. We seek a method of eliminating this unwanted detail and retaining only that part of the information contained in (1.32) which pertains to the properties of a very large system.

There is a very simple method for accomplishing this elimination. We simply replace the  $\omega$  which appears in (1.32) by the complex variable  $z$ . Then (1.32) becomes

$$\begin{aligned} \Sigma(p, z) = & \int \frac{d\omega'}{2\pi} \sum_{p'} |v_q|^2 \\ & \left\{ G^>(p', \omega') \left[ \frac{N_q}{z + \omega_q - \omega'} + \frac{N_q + 1}{z - \omega_q - \omega'} \right] \right. \\ & \left. + G^<(p', \omega') \left[ \frac{N_q}{z - \omega_q - \omega'} + \frac{N_q + 1}{z + \omega_q - \omega'} \right] \right\}_{q=|p-p'|}. \end{aligned} \quad (1.33)$$

By taking  $z$  to have an imaginary part we stand far enough away from the singularities so that we may consider them to be essentially continuously distributed along the real axis. In fact, we may allow them to become continuously distributed by taking the limit as the volume of the system goes to infinity and

$$\sum_{p'} \rightarrow \int \frac{d^3 p'}{(2\pi)^3}. \quad (1.34)$$

Then,  $\Sigma(p, z)$  has the form:

$$\Sigma(p, z) = \int \frac{d\omega}{2\pi} \frac{\Gamma(p, \omega)}{z - \omega} \quad (1.35)$$

with  $\Gamma(p, \omega)$  now being a continuous function of  $\omega$ .

## II. Green's Function Approach

At this point, we shall consider how the results we have just obtained may be rederived by using a more formal Green's function technique. To do this, we define

$$G(r, t; r', t') = \frac{1}{i} \langle T[\psi(r, t)\psi^+(r', t')]\rangle \quad (2.1)$$

where the time variables are limited to be on the imaginary axis with

$$0 < it < \beta ; \quad 0 < it' < \beta .$$

Here  $T$  is a Wick time ordering symbol which tells you to order the operators according to the sense of the "time"  $it$ : the operator with the larger value of  $it$  appearing on the left. Also, for fermions,  $t$  contains a factor of  $(-i)$  for each permutation of the operators from their standard order. Thus,

$$G(r, t; r', t') = \begin{cases} \frac{1}{i} G^>(r, t; r', t') & \text{for } it > it' \\ \pm \frac{1}{i} G^<(r, t; r', t') & \text{for } it < it' . \end{cases} \quad (2.2)$$

The main reason for defining  $G$  for imaginary times lies in the fact that we can relate the values of  $G$  at the two end points of its region of definition by using Eq. (1.16). This implies

$$G(r, t; r', t')|_{t=0} = \pm G(r, t; r', t')|_{t=-i\beta}. \quad (2.3)$$

The boundary condition (2.3) is most conveniently represented by writing  $G$  as a Fourier series in its time variable as

$$G(r, t; r', t') = \int \frac{d^3 p}{(2\pi)^3} \frac{1}{-i\beta} \sum_2 \exp [ip \cdot (r - r') - iz_v(t - t')] G_2(p) . \quad (2.4)$$

This form for  $G$  will necessarily satisfy the boundary condition if

$$z_v = \frac{\pi v}{-i\beta}$$

$$v = \begin{cases} \text{even integer for bosons} \\ \text{odd integer for fermions.} \end{cases}$$

By inverting the Fourier series, one can easily show that the Fourier coefficient is

$$G_v(p) = G(p, z_v) = \int \frac{d\omega}{2\pi} \frac{A(p, \omega)}{z_v - \omega}. \quad (2.5)$$

A useful technique for evaluating  $G$  involves the equation of motion of the annihilation operator:

$$i \frac{\partial \psi(r, t)}{\partial t} = -[H', \psi(r, t)].$$

For free particles this equation of motion is

$$\left[ i \frac{\partial}{\partial t} + \frac{\nabla^2}{2m} + \mu \right] \psi(r, t) = 0.$$

In calculating the time derivative of  $G(r, t; r', t')$ , we use Eq. (2.4) together with the time derivative of the discontinuity at  $it = it'$  produced by the time ordering. This discontinuity is

$$\frac{1}{i} \langle [\psi(r, t)\psi^+(r', t) \mp \psi^+(r', t)\psi(r, t)] \rangle = \frac{1}{i} \delta(r - r').$$

Thus for free particles  $G$  obeys:

$$\left[ i \frac{\partial}{\partial t} + \frac{\nabla^2}{2m} + \mu \right] G(r, t; r', t') = \delta(r - r') \delta(ti - it') i. \quad (2.6)$$

To find  $G(p, z)$  from (2.6), we multiply by  $\exp [ -ip \cdot (r - r') + iz(t - t') ]$  and integrate over all space and all time in the interval  $[0, -i\beta]$ . Then, we find

$$[z_v - \varepsilon_p] G(p, z_v) = 1$$

or

$$G(p, z_v) = \frac{1}{z_v - \varepsilon_p} = \int \frac{a\omega}{2\pi} \frac{A(p, \omega)}{z_v - \omega}.$$

There exists a theorem which states that if an equation that is  $F(z)$  and  $G(z)$  are two analytic functions of  $z$  such that  $F(z) = G(z)$  holds for all

$z_\nu = (\pi\nu - i\beta)$  for even or odd integral  $\nu$  and if  $F(z)$  and  $G(z)$  have no essential singularity at infinity then

$$F(z) = G(z)$$

for all  $z$ . Therefore (2.6) implies

$$\int \frac{d\omega}{2\pi} \frac{A(p, \omega)}{z - \omega} = \frac{1}{z - \varepsilon_p}$$

for all  $z$  and we find

$$A(p, \omega) = 2\pi\delta(\omega - \varepsilon_p)$$

just as before.

To illustrate the application of Green's function techniques, we consider the interaction of electrons with longitudinal phonon, which may be represented by the Hamiltonian

$$H' = H_e + H_p + H_{ep} \quad (2.7a)$$

$$H_e = \int dr \psi^+(r) \left[ \frac{\nabla^2}{2m} - \mu \right] \psi(r) \quad (2.7b)$$

$$H_p = \sum_q \omega_q a_q^\dagger a_q \quad (2.7c)$$

$$H_{ep} = \sum_q v_q a_q \int dr \exp(+iq \cdot r) \psi^+(r) \psi(r) \quad (2.7d)$$

$$+ \sum_q v_q^* a_q^\dagger \int dr \exp(-iq \cdot r) \psi^+(r) \psi(r).$$

Here  $\psi^+(r)$  and  $\psi(r)$  are electron wave field creation and annihilation operators,  $a_q^\dagger$  and  $a_q$  are phonon creation and annihilation operators,  $\omega_q$  is the phonon energy. For simplicity, we ignore Umklapp processes, the possibility of several types of phonons, and the spin of the electrons.

We see immediately that the various operators obey the equations of motion

$$\begin{aligned} & \left[ i \frac{\partial}{\partial t} + \frac{\nabla^2}{2m} + \mu \right] \psi(r, t) \\ &= \sum_q [v_q a_q(t) \exp(iq \cdot r) + v_q^* a_q^\dagger(t) \exp(-iq \cdot r)] \psi(r, t) \end{aligned} \quad (2.8a)$$

$$\left( i \frac{\partial}{\partial t} - \omega_q \right) a_q(t) = \int dr \nu_q^* \exp(iq \cdot r) \psi^+(r, t) \psi(r, t) \quad (2.8b)$$

$$\left( i \frac{\partial}{\partial t} + \omega_q \right) a_q^+(t) = - \int dr \nu_q \exp(-iq \cdot r) \psi^+(t, r) \psi(r, t). \quad (2.8c)$$

It is quite simple to compute the equation of motion of the electronic Green's function. We have:

$$\begin{aligned} \left[ i \frac{\partial}{\partial t} + \frac{\nabla^2}{2m} + \mu \right] G(r, t; r', t') &= \delta(r - r') \delta(t - t') \\ &+ \frac{1}{i} \langle T \left\{ \sum_q [\nu_q a_q(t) \exp(iq \cdot r) \right. \\ &\quad \left. + \nu_q^* a_q^+(t) \exp(-iq \cdot r)] \right. \\ &\quad \left. \psi(r, t) \psi^+(r', t') \right\} \rangle. \end{aligned} \quad (2.9)$$

Therefore, in order to find  $G(l, l')$  we need to know

$$\langle T[a_q(t) \psi(1) \psi^+(1')] \rangle$$

and

$$\langle T[a_q^+(t) \psi(1) \psi^+(1')] \rangle$$

where 1 stands for  $r, t$ , and 1' for  $r', t'$ . These functions are not known, but we can use the equation of motion for  $a_q(t)$  and  $a_q(t')$  to eliminate the phonon variables from these expressions. If we are to make use of these equations of motion, we must allow the time in  $a_q(t)$  and  $a_q^+(t')$  to be different from  $t_1$ , so that we may differentiate with respect to  $t$ . For this reason, we define:

$$F_q(t, 1, 1') = \langle T[a_q(t) \psi(1) \psi^+(1')] \rangle \quad (2.10a)$$

$$\tilde{F}_q(t, 1, 1') = \langle T[a_q^+(t) \psi(1) \psi^+(1')] \rangle. \quad (2.10b)$$

From (2.3b) and (2.3c) we find

$$\begin{aligned} \left[ i \frac{\partial}{\partial t} - \omega_q \right] F_q(t, 1, 1') \\ = \nu_q^* \langle T \left[ \int d\bar{r} \exp(-iq \cdot \bar{r}) \psi^+(\bar{r}, t) \psi(\bar{r}, t) \psi(1) \psi^+(1') \right] \rangle \end{aligned} \quad (2.11a)$$

and

$$\begin{aligned} & \left[ i \frac{\partial}{\partial t} + \omega_q \right] \tilde{F}_q(t, 1, 1') \\ &= -v_q \langle T \left[ \int d\bar{r} \exp(iq \cdot \bar{r}) \psi^+(\bar{r}, t) \psi(\bar{r}, t) \psi(1) \psi^+(1') \right] \rangle. \end{aligned} \quad (2.11b)$$

There are no discontinuity terms coming from differentiating  $T$  because the equal time commutator of  $a_q$  and  $a_q^+$  with  $\psi$  and  $\psi^+$  vanishes.

Equations (2.11) are to be solved with the standard 0 to  $-i\beta$  boundary condition:

$$F_q(t, 1, 1')|_{t=0} = F_q(t, 1, 1')|_{t=-i\beta} \quad (1.16)$$

and similarly for  $F$ . In obtaining the solution to (2.11) it is convenient to use the function  $d_\omega(t, t')$ , which is defined by the differential equation

$$\left[ i \frac{\partial}{\partial t} - \omega_q \right] d_{\omega_q}(t, t') = \delta(t - t') \quad \text{for} \quad \begin{cases} 0 < it < \beta \\ 0 < it' < \beta \end{cases}$$

and the boundary condition:

$$d_{\omega_q}(0, t') = d_{\omega_q}(-i\beta, t').$$

The solution to this equation for  $d_\omega$  may be written down at once. We split  $d_\omega$  into two parts in just the same way as we divided  $G(1, 1')$  into two parts by writing

$$id_{\omega_q}(t_1, t_2) = \begin{cases} d_{\omega_q}^>(t_1, t_2) & \text{for } it_1 > it_2 \\ d_{\omega_q}^<(t_1, t_2) & \text{for } it_1 < it_2. \end{cases} \quad (2.12)$$

We can see immediately that  $d_{\omega_q}^>$  and  $d_{\omega_q}^<$  are exactly analogous to  $G^>(p, t_1 - t_2)$  and  $G^<(p, t_1 - t_2)$  for free bosons if the replacement

$$\left( \frac{p^2}{2m} - \mu \right) \rightarrow \omega$$

is made. Therefore, we have

$$\begin{aligned} d_{\omega_q}^>(t_1 - t_2) &= \exp[-i\omega_q(t_1 - t_2)] (N_q + 1) \\ d_{\omega_q}^<(t_1 - t_2) &= \exp[-i\omega_q(t_1 - t_2)] N_q \end{aligned} \quad (2.13a)$$

where  $N_q$  is the equilibrium number of phonons with wave vector  $\mathbf{q}$ .

$$N_q = \frac{1}{\exp(\beta\omega_q) - 1}.$$

Also, we see

$$\begin{aligned} d_{\omega_q}^>(t_1 - t_2) &= -\exp[i\omega_q(t_1 - t_2)] N_q \\ d_{\omega_q}^<(t_1 - t_2) &= -\exp[i\omega_q(t_1 - t_2)] (N_q + 1) \end{aligned} \quad (2.13b)$$

since

$$\frac{1}{\exp(-\beta\omega_q) - 1} = -\frac{1}{\exp(\beta\omega_q) - 1} - 1 = -(1 + N_q).$$

We can see immediately that solution to Eq. (2.11) with the boundary condition (1.16) may be expressed in terms of  $d$  as:

$$\begin{aligned} F_q(t, 1, 1') &= \int d\bar{r} \int_0^{-i\beta} d\bar{t} v_q^* \exp(-iq \cdot \bar{r}) d_{\omega_q}(t, \bar{t}) \\ &\quad \langle T[\psi^+(\bar{r}, \bar{t}) \psi(\bar{r}, \bar{t}) \psi(1) \psi^+(1')] \rangle \end{aligned} \quad (2.14a)$$

$$\begin{aligned} \tilde{F}_q(t, 1, 1') &= - \int d\bar{r} \int_0^{-i\beta} d\bar{t} v_q \exp(iq \cdot \bar{r}) d_{\omega_q}(t, \bar{t}) \\ &\quad \langle T[\psi^+(\bar{r}, \bar{t}) \psi(\bar{r}, \bar{t}) \psi(1) \psi^+(1')] \rangle. \end{aligned} \quad (2.14b)$$

Notice the great utility of the boundary condition and the  $[0, -i\beta]$  approach. This approach enables us to eliminate all reference to the phonon variables in expressions like  $F_q$  and  $\tilde{F}_q$  and reduce these to expressions which involve only electron operators. Of course, we have to pay a price for this elimination. This price may be seen from the result of substituting (2.14) and back into the equation of motion of (2.6):

$$\begin{aligned} \left[ i \frac{\partial}{\partial t} + \frac{\nabla_1^2}{2m} + \mu \right] G(1, 1') &= \delta(1 - 1') \\ &\quad + \frac{1}{i} \sum_q |v_q|^2 \int d\bar{r} \int_0^{-i\beta} d\bar{t} \\ &\quad [\exp(iq \cdot (r - \bar{r})) d_{\omega_q}(t, \bar{t}) \\ &\quad - \exp(-iq \cdot (\bar{r} - \bar{r})) d_{\omega_q}(\bar{t}, \bar{t}) \\ &\quad \langle T[\psi(1)] \psi^+(1') \psi^+(\bar{r}, \bar{t}) \psi(\bar{r}, \bar{t}) \rangle]. \end{aligned} \quad (2.15)$$

It is convenient to rewrite this expression in terms of

$$G_2(1, 2; 1', 2') = \left( \frac{1}{i} \right)^2 \langle T[\psi(1) \psi(2) \psi^+(2') \psi^+(1')] \rangle \quad (2.16)$$

as

$$\left[ i \frac{\partial}{\partial t} + \frac{V_1^2}{2m} + \mu \right] G(1, 1') = \delta(1 - 1') \quad (2.17)$$

$$\pm i \int d\mathbf{r}_2 \int_0^{-i\beta} dt_2 V(1 - 2) G_2(1, 2; 1', 2)$$

where

$$V(1 - 2) = \sum_q |v_q|^2 [\exp [iq \cdot (\mathbf{r}_1 - \mathbf{r}_2)] d_{\omega_q}(t_1, t_2) \\ \exp [-iq \cdot (\mathbf{r}_1 - \mathbf{r}_2)] d_{-\omega_q}(t_1, t_2)]. \quad (2.18)$$

The reason that Eq. (2.17) is so instructive is that it is quite similar in structure to the equation of motion which would emerge from an ordinary electron-electron interaction. If the ordinary interaction can be represented by a central potential  $v(|\mathbf{r}_1 - \mathbf{r}_2|)$ , then the equation of motion for  $G$  again takes the form (2.13) except for this case:

$$V(1, 2) = \delta(t_1 - t_2) v(|\mathbf{r}_1 - \mathbf{r}_2|). \quad (2.19)$$

Therefore the phonons act to produce an affective electron-electron potential. This potential may be considered to result from the fact that an electron at one point in space and time may change the phonon field by emitting or absorbing phonons. This change in the phonon field can at a later time, scatter electrons at another point in space so that the scattering looks like it is produced by a retarded interaction between electrons.

To find  $G$  from Eq. (2.17), we must make some approximation for the  $G_2(1, 2; 1', 2')$  which appears in that equation. This two-particle Green's function, of course, describes the correlated motion of two electrons added to the system at 1' and 2' and removed at 1 and 2. The simplest possible approximation for this  $G_2$  is to come from the assumption that the added electrons move quite independently of one another. This assumption may be expressed mathematically as

$$G_2(1, 2; 1', 2') \approx G(1, 1') G(2, 2') - G(1, 2') G(2, 1'). \quad (2.20)$$

The appearance of two terms in this expression is a result of Fermi statistics obeyed by the electrons which requires that

$$G_2(1, 2; 1', 2') = -G_2(2, 1; 1', 2').$$

When we substitute (2.20) in (2.17) we find

$$\begin{aligned} \left[ i \frac{\partial}{\partial t} + \frac{V_1^2}{2m} + \mu \right] G(1, 1') &= \delta(1 - 1') \\ &\pm i \left[ \int V(1 - 2) G(1, 2) d2 G(1, 1') \right. \\ &\quad \left. + i \int d2 V(1 - 2) G(1, 2) G(2, 1') \right] \end{aligned} \quad (2.21)$$

the middle term on the right-hand side of (2.21) should be neglected for two reasons:

(a) This term is proportional to

$$\int d2 V(1 - 2) \langle n(2) \rangle = \langle n \rangle \int dr \int_0^{-i\beta} dt V(r, t).$$

After the  $r_2$  integral is performed, this expression becomes proportional to

$$|v_q|^2|_{q=0}.$$

However, a  $q = 0$  phonon is pure nonsense. This "phonon" represents the effect of picking up and bodily displacing the whole crystal. Therefore this whole term is physically meaningless.

(b) This term is proportional to the average potential field produced by all the electrons in the system. As such, it has actually been included in the original definition of the band structure which underlies our original Hamiltonian. Therefore, this term has already been counted and it must now be left out.

After this term is thrown out Eq. (2.21) may be rewritten as:

$$\left[ i \frac{\partial}{\partial t} + \frac{V_1^2}{2m} + \mu \right] G(1, 1') = \delta(1 - 1') + \int d2 \Sigma(1, 2) G(2, 1') \quad (2.22)$$

where the self-energy  $\Sigma$  is

$$\Sigma(1, 1') = iV(1 - 1') G(1, 1'). \quad (2.23)$$

It is a trivial matter to verify that  $\Sigma(1, 1')$  obeys the same boundary conditions as  $G$ , i.e.,

$$\Sigma(1, 1')|_{t_1=0} = -\Sigma(1, 1')|_{t_1=i\beta} \quad (2.24)$$

since  $V(1, 1')$  obeys the boson boundary condition

$$V(1, 1')|_{t_1=0} = V(1, 1')|_{t_1=-i\beta}.$$

Since  $\Sigma$  obeys the same boundary condition as  $G$ , its formal properties are very similar to the formal properties of  $G$ . For example, when  $\Sigma(1, 1')$  is split into two parts as

$$i\Sigma(1, 1') = \begin{cases} \Sigma^>(1 - 1') = \int \frac{d^3 p}{(2\pi)^3} \frac{d\omega}{2\pi} \\ \cdot \exp [ip \cdot (r_1 - r_2) - i\omega(t_1 - t_1')] \Sigma^>(p, \omega) \text{ for } it_1 > it_1' \\ -\Sigma^<(1 - 1') = -\int \frac{d^3 p}{(2\pi)^3} \frac{d\omega}{2\pi} \\ \cdot \exp [ip \cdot (r_1 - r_1') - i\omega(t_1 - t_1')] \Sigma^<(p, \omega) \text{ for } it_1 < it_1' \end{cases} \quad (2.25)$$

then  $\Sigma^>(p, \omega)$  and  $\Sigma^<(p, \omega)$  obey the detailed balancing relation

$$\Sigma^<(p, \omega) = \exp(-\beta\omega) \Sigma^>(p, \omega);$$

also,  $\Sigma$  may be written as a Fourier series

$$\Sigma(1, 1') = \int \frac{d^3 p}{(2\pi)^3} \exp [ip \cdot (r_1 - r_1')] \frac{1}{-i\beta} \sum_v \exp [-iz_v(t_1 - t_1')] \Sigma_v(p) \quad (2.26)$$

with the Fourier coefficient given by

$$\Sigma_v(p) = \Sigma(p, z_v) = \int \frac{d\omega}{2\pi} \frac{\Sigma^>(p, \omega) + \Sigma^<(p, \omega)}{z_v - \omega} = \int \frac{d\omega}{2\pi} \frac{\Gamma(p, \omega)}{z_v - \omega}. \quad (2.27)$$

This Fourier series representation of  $\Sigma(1, 1')$  is very convenient because it enables us to solve the differential Equation (2.22) quite directly.

If we multiply this equation by  $\exp[-ip \cdot (r_1 - r_1') + iz_v(t_1 - t_1')]$  and then integrate over all  $r_1$  and all  $t_1$  in the interval  $0 < it_1 < \beta$ , then (2.22) becomes

$$[z_r - \varepsilon_p - \Sigma(p, z_v)] G(p, z_v) = 1. \quad (2.28)$$

Equation (2.28) is a relation between the analytic functions

$$\Sigma(p, z) = \int \frac{d\omega}{2\pi} \frac{\Sigma^>(p, \omega) + \Sigma^<(p, \omega)}{z - \omega} = \int \frac{d\omega}{2\pi} \frac{I(p, \omega)}{z - \omega} \quad (2.29a)$$

$$G(p, z) = \int \frac{d\omega}{2\pi} \frac{G^>(p, \omega) + G^<(p, \omega)}{z - \omega} = \int \frac{d\omega}{2\pi} \frac{A(p, \omega)}{z - \omega} \quad (2.29b)$$

which is known to hold on all the points

$$z = z_v = \frac{\pi v}{-i\beta} \quad v = \text{odd integer.}$$

From the fact that this relation holds on this limited set of points and the fact that neither  $\Sigma(p, z)$  nor  $G(p, z)$  has an essential singularity at  $\infty$  it follows that (2.28) holds for all  $z$ , i.e., that

$$G(p, z) = \frac{1}{z - \varepsilon_p - \Sigma(p, z)}. \quad (2.30)$$

In order to make use of Eq. (2.30) we use (2.18) and (2.23) to write

$$\begin{aligned} \Sigma^>(1, 1') &= V^>(1, 1') G^>(1, 1') \\ &= \sum_q |v_q|^2 \exp[iq \cdot (r_1 - r_1')] d_{\omega_q}(t_1 - t_1') \\ &\quad - \exp[-iq \cdot (r_1 - r_1')] d_{-\omega_q}(t_1 - t_1') G^>(1, 1'). \end{aligned} \quad (2.31)$$

The Fourier transform of (2.31) is

$$\begin{aligned} \Sigma^>(p, \omega) &= \int \frac{d^3 p'}{(2\pi)^3} \frac{d\omega'}{2\pi} G^>(p', \omega') \{ |v_q|^2 [N_q 2\pi \delta(\omega + \omega_q - \omega')] \\ &\quad + (N_q + 1) 2\pi \delta(\omega - \omega_q - \omega') \} \} \quad q = |p - p'|. \end{aligned} \quad (2.32a)$$

A similar evaluation gives

$$\begin{aligned} \Sigma^<(p, \omega) = & \int \frac{d^3 p'}{(2\pi)^3} \frac{d\omega'}{2\pi} G^<(p', \omega') \{ |v_q|^2 [(N_q + 1)2\pi\delta(\omega + \omega_q - \omega')] \\ & + N_q 2\pi\delta(\omega - \omega_q - \omega') \} \} \quad q = |p - p'|. \end{aligned} \quad (2.32b)$$

The substitution of (2.32) into (2.29a) leads back to our earlier result (1.33):

$$\begin{aligned} \Sigma(p, z) = & \int \frac{d\omega'}{2\pi} \int \frac{d^3 p'}{(2\pi)^3} |v_q|^2 \\ & \cdot \left\{ G^>(p', \omega') \left[ \frac{N_q}{z + \omega_q - \omega'} + \frac{N_q + i}{z - \omega_q - \omega'} \right] \right. \quad (2.33) \\ & \left. + G^<(p', \omega') \left[ \frac{N_q}{z - \omega_q - \omega'} + \frac{N_q + 1}{z + \omega_q - \omega'} \right] \right\} \quad q = |p - p'|. \end{aligned}$$

It is now quite simple to derive an expression for  $A(p, \omega)$  since  $iA(p, \omega)$  is the discontinuity in  $G(p, z)$  as  $z$  crosses the real axis. From (2.30),

$$A(p, \omega) = \frac{\Gamma(p, \omega)}{[\omega - \epsilon_p - \text{Re } \Sigma(p, \omega)]^2 + [\Gamma(p, \omega)/2]^2}. \quad (2.34)$$

Here  $\text{Re } \Sigma(p, \omega)$  is the part of  $\Sigma(p, z)$  which is continuous as  $z$  crosses the real axis. It is given by an expression identical with (2.33) except that

$$\frac{1}{z \pm \omega_q - \omega'} \rightarrow P \frac{1}{\omega \pm \omega_q - \omega'}$$

where  $P$  stands for principal value.  $\Gamma(p, \omega)$  is the discontinuity in (2.33). In  $\Gamma$ , the energy denominators in (2.33) are replaced by  $\delta$ -functions:

$$\frac{1}{z \pm \omega_q - \omega'} \rightarrow 2\pi\delta(\omega \pm \omega_q - \omega').$$

Since  $A(p, \omega)$  is defined in terms of  $G^>$  and  $G^<$  by (2.29b) and  $\Sigma(p, z)$  is defined in terms of  $G^>$  and  $G^<$  by (2.33), Eq. (2.34) gives us one relation between  $G^>$  and  $G^<$ . The boundary condition

$$G^<(p, \omega) = \exp(-\beta\omega) G^>(p, \omega) \quad (2.35)$$

provides another relation between  $G^>$  and  $G^<$ . Thus, we have two equations in two unknowns and we may solve for  $G^>$  and  $G^<$ .

### III. Specialization to a Metal

At this point, I would like to quote two rather surprising facts about the approximation described above:

- (a) This approximation is exact in a normal (nonsuperconducting) metal if the correct phonon energy spectrum is employed and the electron-electron interactions are neglected.
- (b) The highly nonlinear equations we have written down are exactly soluble for a metal.

These statements have been proved by Midgal (8). Before outlining Midgal's proof, I should point out that these statements are very closely related to the well-known fact that the adiabatic approximation (9) gives a correct description of the electron-phonon interaction in metals. Therefore, I and II really tell us that our Green's function approximation is a correct restatement of the adiabatic approximation.

In order to see the essence of Midgal's arguments, let us consider the diagrammatic expansion for the self-energy in a power series in  $G$  and  $V$ . The terms we have considered in the self-energy correspond to the diagrams

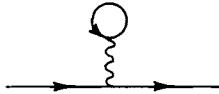


FIG. 3

$$\Sigma_1(1, 1') = \delta(1 - 1') [-i \int d2 V(1 - 2) G(2, 2)] \quad (3.1)$$

and

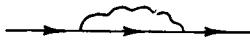


FIG. 4

$$\Sigma_2(1, 1') = iV(1, 1') G(1, 1'). \quad (3.2)$$

Here the  $\longrightarrow$  line stands for a  $G$  and  $\sim\sim$  for the interaction  $V$ . The first of these terms vanishes and the next is the one we have taken into account.

The next order terms, which we have neglected are:

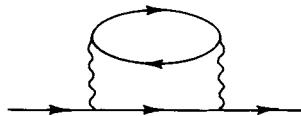


FIG. 5

$$\Sigma_3(1, 1') = i\delta V(1, 1') G(1, 1') \quad (3.3)$$

$$\delta V(1, 1') = -i \int V(1, 2) G(2, 2') G(2', 2) V(2', 1') d2' d2$$

and

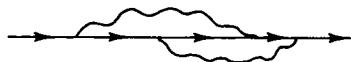


FIG. 6

$$\Sigma_4(1, 1') = i^2 \int d2 d2' V(1, 2) G(1, 2') G(2', 2) G(2, 1') V(2, 1'). \quad (3.4)$$

The substance of point I in the Migdal paper is that terms like  $\Sigma_4$  are negligible while terms like  $\Sigma_3$  serve to shift the phonon energies in the  $V(1, 1')$  of  $\Sigma_2$  from the bare phonon energies to the energies of the fully interacting phonon system. The manner in which  $\Sigma_3$  serves to shift the energies is, I think, clear. However, some further discussion is necessary in order to see why  $\Sigma_4$  is small.

A crucial fact in this discussion is that only electrons with very small values of  $\epsilon_p$  ( $\epsilon_p \ll \mu$ ) play any role in the electron-phonon interaction. The reason for this limitation lies in the fact that the phonon energies are all quite small, in fact,

$$(\omega_q/\mu) \sim \sqrt{\frac{m}{M}} \ll 1 \quad (3.5)$$

where  $m$  is the electronic mass and  $M$  the ionic mass. Therefore, an electron which initially lies quite close to the Fermi surface must always

remain quite close to  $\varepsilon_p \approx 0$ . If all electronic momenta must be very close to

$$p = p_F = \sqrt{2m\mu}.$$

This puts considerable restrictions on the momentum integrals which are to be done in evaluating  $\Sigma_4$ . In fact, this phase space restriction leads to  $\Sigma_4$  being smaller than  $\Sigma_2$  by a factor of order  $\sqrt{m/M}$ . (We assume that the dimensionless coupling constant  $[|v_q|^2 mp_F/\omega_q]$  is of order unity.)

In this way, Migdal proved that the approximation that we discussed in the last two sections was an exact perturbation theoretic expansion of the self-energy to order  $(m/M)^{1/2}$ . Migdal apparently did not publish this proof for several years because it obviously contained a grave defect—it appears to prove that the electron-phonon interaction has nothing to do with superconductivity. The trouble is that, for a superconductor, perturbation theory does not converge. Hence this whole perturbation theoretic argument is quite wrong for a superconductor.

We shall return to the discussion of the superconductor later. For now let us consider Migdal's second point. We can solve (2.34) for  $A(p, \omega)$ . To effect this solution we examine (2.33) and notice that  $\Sigma(p, z)$  is a very slowly varying function of  $p$ , but a rapidly varying function of  $z$ . The rate of variation in  $z$  is measured by  $\omega_q$  but the rate of variation in  $\varepsilon_p = (p^2/2m - \mu)$ , is measured by  $\mu$ . Because of his slow variation in  $p$ , we can simply set  $p = p_F$  in Eq. (2.33) and write (2.34) as

$$A(p, \omega) = \frac{\Gamma(\omega)}{[\omega - \varepsilon_p - \operatorname{Re} \Sigma(\omega)]^2 + [\Gamma(\omega)/2]^2} \quad (3.6)$$

with

$$\operatorname{Re} \Sigma(\omega) = \operatorname{Re} \Sigma(p_F, \omega)$$

$$\Gamma(\omega) = \operatorname{Re} \Gamma(p_F, \omega).$$

Let us observe that (3.6) implies

$$\int \frac{d\varepsilon}{2\pi} A(p, \omega) = 1. \quad (3.7)$$

Equation (3.7) is crucially important because a huge variety of physical quantities depend upon the integral (3.7). Because this integral is in-

dependent of the strength of the electron-phonon interaction, a whole host of calculations are immensely simplified. The physical meaning of (3.7) can be roughly appreciated if we notice that the electron-phonon interaction serves to scatter electrons only over the very narrow range of momenta

$$\left| \frac{p^2}{2m} - \mu \right| \lesssim \omega_q .$$

That is to say the interaction produces a quasi-particle state by redistributing the electron momenta and superposing states of slightly different electronic momentum. However, when we examine a sum over all  $p$  (or equivalently, all  $\epsilon$ ) all this redistribution becomes irrelevant so that the integral in (3.7) is quite independent of the strength of electron-phonon interaction.

Equation (3.7) can be used to simplify the expression (2.33) for  $\Sigma(p, z)$ . This simplification is effected by writing

$$\int \frac{d^3 p}{(2\pi)^3} = \int d\varepsilon_p \int \frac{d\Omega}{4\pi} \frac{mp}{2\pi^2} \approx \frac{mp_F}{2\pi^2} \int d\varepsilon \int \frac{d\Omega}{4\pi} \quad (3.8)$$

where

$$\Omega = \vec{p}/|\vec{p}| \approx p/p_F .$$

We shall employ the abbreviation

$$N(0) = \frac{mp_F}{2\pi^2} \quad (3.9)$$

for the (unperturbed) density of states in energy at the Fermi surface. Then by using the relations

$$G^>(p, \omega) = [1 + f(\omega)] A(p, \omega)$$

$$G^<(p, \omega) = f(\omega) A(p, \omega) ,$$

we can rewrite Eq. (2.33) as

$$\begin{aligned} \Sigma(z) &= N(0) \int d\omega' \int \frac{d\Omega'}{4\pi} |\nu_q|^2 \\ &\cdot \left\{ [1 + f(\omega')] \left[ \frac{N_q}{z + \omega_q - \omega'} + \frac{N_q + 1}{z - \omega_q - \omega'} \right] \right. \end{aligned} \quad (3.10)$$

$$\begin{aligned}
& + f(\omega') \left[ \frac{N_q}{z - \omega_q - \omega'} + \frac{N_q + 1}{z + \omega_q - \omega'} \right] \} \\
& \cdot \int \frac{d\varepsilon'}{2\pi} A(\varepsilon', \omega') . \quad q = p_F |\Omega - \Omega'| \tag{3.10 cont.}
\end{aligned}$$

Since the  $\varepsilon'$  integral of  $A$  is unity according to (3.7), we have reduced the evaluation of  $\Sigma(z)$  and hence  $A(p, \omega)$  to quadratures. Schrieffer and Englesberg (10) have done these integrals at zero temperature and examined the form of  $A$ .

However, for most purposes it is not even necessary to know  $A$ : the sum rule (3.7) is quite sufficient for obtaining a variety of useful results. For example, consider a tunneling experiment: We can rewrite expression (1.12) for the tunneling rate as

$$\begin{aligned}
\text{net } \frac{dN}{dt} &= 2 \int \frac{d\omega}{2\pi} \int \frac{d\omega'}{2\pi} \int \frac{d^3 p}{(2\pi)^3} \int \frac{d^3 p'}{(2\pi)^3} \\
&\cdot |T(p, p')|^2 A_A(p, \omega) A_B(p', \omega') \\
&\cdot 2\pi\delta(\omega - \omega' + eV) [f(\omega) - f(\omega')] . \tag{3.11}
\end{aligned}$$

(The factor 2 is a result of the sum over electron spins.) Then we can use the fact that  $T(p, p')$  depends only very weakly upon  $\varepsilon$  and  $\varepsilon'$  to do the  $\varepsilon$  and  $\varepsilon'$  integrals in (3.11). The result

$$\begin{aligned}
\text{net } \frac{dN}{dt} &= 2[N(0)]^2 2\pi \int \frac{d\Omega'}{4\pi} \int \frac{d\Omega'}{4\pi} |T(p_F\Omega, p_F\Omega')|^2 \\
&\cdot \int d\omega \int d\omega' \delta(\omega - \omega' + eV) [f(\omega) - f(\omega')] \\
&= 2[N(0)]^2 2\pi \int \frac{d\Omega}{4\pi} \int \frac{d\Omega'}{4\pi} |T(p_F\Omega, p_F\Omega')|^2 eV \tag{3.12}
\end{aligned}$$

is very interesting because all effects of the electron-phonon interaction have completely cancelled out.

Notice, incidentally, the complete failure of the conventional quasi-particle picture which gives the effective density of states in energy as

$$N(0) \frac{d\varepsilon}{dE} \tag{3.13}$$

with  $E$  given by

$$E_p = \varepsilon_p + \Sigma(p, E_p). \quad (3.14)$$

Even for regions of  $E$  in which  $\Sigma(p, E)$  is completely real so that the quasi particles are infinitely long-lived expression (3.13) is irrelevant. The relevant density of states for tunneling is the simpler expression  $N(0) = mp_F/2\pi^2$ .

#### IV. The Superconductor

All of the arguments of the previous lectures can be generalized to the case of the superconductor. This generalization requires the use of the additional propagators

$$F(1, 2) = \frac{1}{i} \langle T[\psi_\uparrow(1) \psi_\downarrow(2)] \rangle \quad (4.1)$$

and

$$F^+(1, 2) = \frac{1}{i} \langle T[\psi_\downarrow^+(1) \psi_\uparrow^+(2)] \rangle, \quad (4.2)$$

which respectively describe processes in which a bound pair breaks up so that two particles may be removed from the system and processes in which two particles added to the system form a bound pair. (The formulation given here is appropriate in the case in which the pairs are bound in an  $S$  state of zero total spin. In more complex situations, more correlation functions need be considered. See the work of R. Balian in this volume.)

It is important that  $F$  and  $F^+$  be considered handled in exactly the same way as  $G$ . Nambu<sup>4</sup> (11) has introduced a simple trick for handling  $G$ ,  $F$ , and  $F^+$  at the same time. He begins with the spinor fields

$$\Psi(1) = \begin{pmatrix} \psi_\uparrow(1) \\ \psi_\downarrow(1) \end{pmatrix}; \quad \Psi^+(1) = \overbrace{\psi_\downarrow^+(1') \psi_\uparrow^+(1')} \quad (4.3)$$

and notices that the basic Hamiltonian may be rewritten in terms of

<sup>4</sup> Nambu's formalism provides a very convenient technique for extending the B.C.S. theory (12) to the case of retarded interactions.

these fields. For example, the kinetic energy is:

$$\begin{aligned} K.E. &= \int dr \left\{ \left( \frac{\nabla \cdot \nabla'}{2m} - \mu \right) [\psi_{\uparrow}^+(r') \psi_{\uparrow}(r) + \psi_{\downarrow}^+(r') \psi_{\downarrow}(r)] \right\}_{r'=r} \\ &= \int dr \left\{ \left( \frac{\nabla \cdot \nabla'}{2m} - \mu \right) [\psi_{\uparrow}^+(r') \psi_{\uparrow}(r) - \psi_{\downarrow}^+(r') \psi_{\downarrow}(r) + \delta(r-r')] \right\}_{r'=r} \end{aligned}$$

The  $\delta$ -function term is quite irrelevant since it is just a number added to the Hamiltonian. When this term is neglected the kinetic energy can be written in terms of an inner product of the spinors

$$K.E. = \int dr \left\{ \left( \frac{\nabla \cdot \nabla'}{2m} - \mu \right) [\Psi^+(r') \tau_3 \Psi(r)] \right\}_{r'=r} \quad (4.4)$$

Here  $\tau_3$  is the standard Dirac spin matrix

$$\tau_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

Similarly, the interaction term can be written in terms of  $\Psi^+$  and  $\Psi$  as

$$\begin{aligned} H_{ep} &= \int dr [\nu_q a_q \exp(iq \cdot r) + \nu_q^* a_q^+ \exp(-iq \cdot r)] \\ &\quad [\psi_{\uparrow}^+(r) \psi_{\uparrow}(r) + \psi_{\downarrow}^+(r) \psi_{\downarrow}(r)] \\ &\rightarrow \int dr [\nu_q a_q \exp(iq \cdot r) + \nu_q^* a_q^+ \exp(-iq \cdot r)] [\Psi^+(r) \tau_3 \Psi(r)]. \end{aligned} \quad (4.5)$$

The properties of the superconductor are described by a spinor Green's function

$$\begin{aligned} g(1, 1') &= \frac{1}{i} \langle T[\Psi(1) \Psi^+(1')] \rangle \\ &= \begin{pmatrix} G(1, 1') & F(1, 1') \\ F^+(1, 1') & -G(1', 1) \end{pmatrix}. \end{aligned} \quad (4.6)$$

Since this spinor function obeys the same boundary condition as  $G$ , it has exactly the same formal properties as  $G$ . In particular, we can notice that it can be expanded in Fourier series with matrix Fourier coefficients  $g(p, z_r)$  where

$$g(p, z) = \int \frac{d\omega}{2\pi} \frac{a(p, \omega)}{z - \omega} = \int \frac{d\omega}{2\pi} \frac{g^>(p, \omega) + g^<(p, \omega)}{z - \omega}. \quad (4.7)$$

The two pieces of  $g$  are again related by

$$g^<(p, \omega) = \exp(-\beta\omega) g^<(p, \omega). \quad (4.8)$$

Equivalently, we can write

$$\begin{aligned} g^<(p, \omega) &= f(\omega) a(p, \omega) \\ g^<(p, \omega) &= [1 - f(\omega)] a(p, \omega), \end{aligned} \quad (4.9)$$

where  $a(p, \omega)$  is now a matrix.

We can express

$$g(p, z) = \frac{1}{z - \varepsilon_p - \sigma(p, z)} = \int \frac{d\omega}{2\pi} \frac{a(p, \omega)}{z - \omega} \quad (4.10)$$

where the matrix  $\sigma(p, z)$  is expandable in exactly the same kind of perturbation theory as in the normal state. The only difference lies in the fact that the matrix  $g$  replaces the scalar  $G$  and a factor of  $\tau_3$  appears at each vertex. Thus, in lowest order

$$\begin{aligned} \sigma(1, 1') &= \\ &= i V(1 - 1') \tau_3 g(1, 1') \tau_3 \end{aligned} \quad (4.11)$$

or

$$\begin{aligned} \sigma(p, z) &= \int \frac{d^3 p'}{(2\pi)^3} \frac{d\omega'}{2\pi} |\nu_q|^2 \\ &\cdot \left\{ \tau_3 g^>(p', \omega') \tau_3 \left[ \frac{N_q}{z + \omega_q - \omega'} + \frac{N_q + 1}{z - \omega_q - \omega'} \right] \right. \\ &\left. + \tau_3 g(p', \omega') \tau_3 \left[ \frac{N_q}{z - \omega_q - \omega'} + \frac{N_q + 1}{z + \omega_q - \omega'} \right] \right\}. \end{aligned} \quad (4.12)$$

Before we go any further, we should notice that, as in the normal metal,  $\sigma(p, z)$  can be considered to be independent of  $p$ . Hence, we write  $\sigma(p, z) \approx \sigma(p_F, z) = \sigma(z)$ .

In order to solve  $g(p, z)$  we guess the form of the answer for  $\sigma(p, z)$ .

Our guess, which we verify below, is that  $\sigma(p, z)$  contains no contribution proportional to  $\tau_3$  and none proportional to  $\tau_2$ , but only terms proportional to the unit matrix

$$1 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

and

$$\tau_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}.$$

Thus we write

$$\sigma(z) = \sigma_0(z) 1 + \sigma_1(z) \tau_1. \quad (4.13)$$

Actually it is slightly more convenient to express  $\sigma(p, z)$  in terms of the variables

$$\begin{aligned} Z(z) &= [1 - \sigma_0(z)/z] \\ Z(z) \Delta(z) &= \sigma_1(z) \end{aligned} \quad (4.14)$$

with this redefinition of the variables, Eq. (4.10) becomes

$$\begin{aligned} g(p, z) &= \frac{1}{Z(z)z - \varepsilon\tau_3 - \Delta(z)Z(z)\tau_1} \\ &= \frac{zZ(z) + \varepsilon\tau_3 + \Delta(z)Z(z)\tau_1}{Z^2(z) [z^2 - \Delta^2(z)] - \varepsilon^2} \end{aligned} \quad (4.15)$$

and<sup>5</sup>

$$\int \frac{d\varepsilon}{2\pi} g(p, z) = \frac{z + \Delta(z)\tau_1}{\sqrt{-z^2 + [\Delta(z)]^2}} = \int \frac{d\varepsilon}{2\pi} \int \frac{d\omega}{2\pi} \frac{a(p, \omega)}{z - \omega}. \quad (4.16)$$

Here, the sign of the square root is chosen so that as  $z \rightarrow \infty$  below the real axis  $\sqrt{-z^2} \rightarrow -iz$ , while as  $z \rightarrow \infty$  above the real axis  $\sqrt{-z^2} \rightarrow +iz$ . There is a branch line in the definition of the square root along the real axis. The  $\varepsilon$  integral of  $a(p, \omega)$  is now easily computed in terms of the discontinuity of Eq. (4.16) as  $z$  crosses the real axis. This gives

$$\int \frac{d\varepsilon}{2\pi} a(p, \omega) = \text{Re} \frac{\omega + \Delta(\omega)\tau_1}{\sqrt{\omega^2 - [\Delta(\omega)]^2}} \quad (4.17)$$

<sup>5</sup> The first application of this  $\varepsilon$  integration trick to the superconductor appeared in P. Morel and P. W. Anderson (13).

where the square root is defined by the statement

$$\lim_{\omega \rightarrow \infty} \left\{ \omega / \sqrt{\omega^2 - [\Delta(\omega)]^2} \right\} = 1. \quad (4.12)$$

Now we return to Eq. (4.12). We make the substitution  $g^> = (1-f)a$ ,  $g^< = fa$ , and write the momentum integral as

$$\int \frac{d^3 p'}{(2\pi)^3} \rightarrow N(0) \int d\varepsilon' \int \frac{d\Omega'}{4\pi},$$

after the  $\varepsilon'$  integral is performed with the aid of Eq. (4.17), we find

$$\begin{aligned} \sigma(z) &= z[1 - Z(z)] 1 + Z(z) \Delta(z) \tau_1 \\ &= \int d\omega' \operatorname{Re} \left[ \frac{\omega' 1 - \Delta(\omega') \tau_1}{\sqrt{\omega'^2 - [\Delta(\omega')]^2}} \right] K(z, \omega') \end{aligned} \quad (4.18)$$

where

$$\begin{aligned} K(z, \omega') &= N(0) \int \frac{d\Omega'}{4\pi} |\nu_q|^2 \\ &\quad \left\{ \frac{N_q[1 - f(\omega')] + N_q + 1)f(\omega')}{z + \omega_q - \omega'} \right. \\ &\quad \left. + \frac{(N_q + 1)[1 - f(\omega')] + N_q f(\omega')}{z - \omega_q - \omega'} \right\}_{q=p_F|\Omega-\Omega'|} \end{aligned} \quad (4.19)$$

We see that our original assumption, Eq. (4.13) about the form of  $\sigma(z)$  is indeed justified.

It is interesting to note that Eq. (4.18) may be reduced to an integral equation for  $\Delta$  alone since

$$Z(z) = 1 - \frac{1}{z} \int d\omega' \omega' \operatorname{Re} \frac{1}{\sqrt{\omega'^2 - [\Delta(\omega')]^2}} F(z, \omega') \quad (4.20)$$

so that

$$\begin{aligned} \Delta(z) &= - \int d\omega' [K(z, \omega')] \\ &\quad \left\{ \operatorname{Re} \frac{\Delta(\omega')}{\sqrt{\omega'^2 - \Delta(\omega')^2}} - \frac{\Delta(z)\omega'}{z} \operatorname{Re} \frac{1}{\sqrt{\omega'^2 - [\Delta(\omega')]^2}} \right\}. \end{aligned} \quad (4.21)$$

An equation essentially similar to this one has been solved by J.R. Schrieffer *et al.* (14) in the zero temperature limit. The only modification

in this work beyond the formulas indicated here is the appearance of a pseudopotential in  $K(z, \omega')$  which is introduced as a representation of the coulomb potential between electrons.

This solution can be used to describe the tunneling characteristics of a junction between a normal metal and a superconductor. We again use Eq. (3.11)

$$\begin{aligned} \frac{dN}{dt} \Big|_{A \rightarrow B} &= 2[N(0)] \int \frac{d\Omega}{4\pi} \int \frac{d\Omega'}{4\pi} |T(p, p')|^2 \\ &\quad \int \frac{d\omega}{2\pi} \int \frac{d\omega'}{2\pi} 2\pi\delta(\omega - \omega' + eV) [f(\omega) - f(\omega')] \\ &\quad \int d\varepsilon A_A(\varepsilon, \omega) \int d\varepsilon' A_B(\varepsilon', \omega') \end{aligned} \quad (3.11)$$

for the case in which  $A$  is a superconductor and  $B$  a normal metal. Just as before, we employ

$$\int d\varepsilon' A_B(\varepsilon', \omega') = 2\pi.$$

For the superconductor, Eq. (4.16) implies

$$\int d\varepsilon a(\varepsilon, \omega) = 2\pi \operatorname{Re} \left\{ \frac{z + A(z) \tau_1}{\sqrt{z^2[A(z)]^2}} \right\}_{z=\omega}. \quad (4.22)$$

Since the scalar  $A(p, \omega)$  is the upper left-hand corner of matrix  $a(p, \omega)$

$$\int d\varepsilon A_A(\varepsilon, \omega) = 2\pi \operatorname{Re} \frac{\omega}{\sqrt{\omega^2 - [A(\omega)]^2}}. \quad (4.23)$$

[This expression for the density of states was first derived by Schieffer *et al.* (14).]

In this way, we find that the tunneling rate is given by

$$\begin{aligned} \frac{dN}{dt} \Big|_{A \rightarrow B} &= 4\pi[N(0)]^2 \int \frac{d\Omega}{4\pi} \int \frac{d\Omega'}{4\pi} |T(p, p')|^2 \\ &\quad \int d\omega \int d\omega' \delta(\omega - \omega' + eV) [f(\omega) - f(\omega')] \\ &\quad \operatorname{Re} \frac{\omega}{\sqrt{\omega^2 - [A(\omega)]^2}} \end{aligned} \quad (4.24)$$

at zero temperature

$$f(\omega) = \begin{cases} 1 & \text{for } \omega < 0, \\ 0 & \text{for } \omega > 0 \end{cases}$$

so that

$$\left. \frac{dN}{dt} \right|_{A \rightarrow B} \sim \int_{-\epsilon V}^0 d\omega \operatorname{Re} \frac{\omega}{\sqrt{\omega^2 - [\Delta(\omega)]^2}}. \quad (4.25)$$

Therefore, we see that the tunneling rate, expressed as a function of voltage, directly measures

$$\operatorname{Re} \frac{\omega}{\sqrt{\omega^2 - [\Delta(\omega)]^2}}. \quad (4.26)$$

In ref. (14) this quantity is evaluated theoretically and compared with the experiment of J. M. Rowell *et al.* (15) which measures the tunneling rate in a junction composed of superconducting AlPb and normal Al. The agreement between theory and experiment is quite impressive.

It should be noticed that the effective density of states for tunneling is

$$N(0) \operatorname{Re} \frac{\omega}{\sqrt{\omega^2 - [\Delta(\omega)]^2}} = \frac{mp_F}{2\pi^2} \operatorname{Re} \frac{\omega}{\sqrt{\omega^2 - [\Delta(\omega)]^2}}. \quad (4.27)$$

This is very different from the expression for the density of states which emerges from the quasi-particle picture. The latter is

$$N(0) \frac{d\varepsilon}{dE}$$

where the quasi-particle energy is given by

$$E^2 = \varepsilon^2 + [\Delta(E)]^2$$

and hence

$$\begin{aligned} \frac{d\varepsilon}{dE} &= \frac{1}{\varepsilon} \left[ E - \Delta(E) \frac{d\Delta(E)}{dE} \right] \\ &= \frac{E}{\sqrt{E^2 - [\Delta(E)]^2}} - \frac{\Delta(E) \frac{d\Delta(E)}{dE}}{\sqrt{E^2 - [\Delta(E)]^2}}. \end{aligned}$$

Consequently, the quasi-particle picture gives an effective tunneling density of states as

$$N(0) \left[ \frac{E}{\sqrt{E^2 - [\Delta(E)]^2}} - \frac{\Delta(E) \frac{d\Delta(E)}{dE}}{\sqrt{E^2 - [\Delta(E)]^2}} \right]. \quad (4.28)$$

Whenever  $\Delta(E)$  depends upon  $E$  the quasi-particle picture gives a density of states different from the exact expression, Eq. (4.27). Therefore, the quasi-particle picture fails whenever  $\Delta(E)$  depends upon  $E$ .

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# **Special Effects in Superconductivity**

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## **I. Introduction**

There are generally considered to be two basic approaches to many-body problems — in fact to any problems of theoretical physics: the microscopic approach from the ground up, and phenomenology. However, in actual fact, physics does not progress very rapidly if either of these is pursued to the exclusion of the other. Phenomenology, of course, can never really explain anything but can merely describe; while Schrödinger's equation and rigorous mathematical theory can never hope to deal successfully with the complexities of real physical systems but only with mathematical oversimplifications like the free-electron gas, the hard-sphere Bose fluid, or the Heisenberg ferromagnet. And results, at that, are usually conditional on the convergence of a divergent perturbation series. The most successful approach to physics—in most cases the only successful approach—is probably the judicious combination of phenomenology with microscopic theory, and of experiment with both.

What this has to do with superconductivity is this: it is naïve to hope to prove “from the ground up” that (say) pure tin is a superconductor, obeying the B.C.S. theory with some improvements, since we cannot *prove* either that it is a solid or a metal, much less calculate its phonon spectrum and band structure; besides, we never deal with the infinite specimens of mathematically pure, undeformed tin which mathematical theory describes.

We can reach a much greater degree of certainty and understanding by accepting a reasonable model for tin containing as few phenomenological parameters as possible as well as microscopic theoretical insights, and seeing to what extent such a model correlates quantitative and

qualitative experimental results. From this kind of approach we can arrive at a degree of understanding of phenomena which amounts to certainty. I know this kind of reasoning is somewhat uncomfortable to the school of "pure" many-body theory which has arisen in the past 6 or 7 years, but the fact remains that it is to it and not to pure theory that we owe our feeling of certainty that we understand such phenomena as the very regularity of solids, normal metallic behavior, ferro- and antiferromagnetism, and so on.

Superconductivity, I believe, belongs also in this category of phenomena of whose basic nature we are virtually certain, primarily because of the wide variety of phenomena which can be correlated by one form or another of B.C.S. theory. This is why I think it is important to discuss "special effects" in a school such as this: because they do in fact provide the acid test of a many-body theory.

There are three kinds of effects, each of which is especially important for a different reason. The Josephson effect is important because, besides depending in a crucial way on the coherence properties of the wavefunction, it makes contact with some extremely general questions about many-body theory and symmetry properties of condensed states.

The scattering effects of impurities of various kinds are important because they test, in the most direct way possible, the precise nature of the condensation responsible for superconductivity. The impurity effect was, to me, the first completely convincing evidence for the B.C.S. theory.

Finally, hard superconductivity is the area in which the most characteristic properties of superconductivity come into question: namely the persistent current, flux quantization, and superfluidity properties. Here, in contrast to the previous two, phenomenology is important and it is the Landau-Ginzburg phenomenological theory which plays the major role.

We shall discuss here only the first, the Josephson effect.<sup>1</sup>

<sup>1</sup> For material on the last effect, hard superconductivity, see Notes from the 1963 Summer School of Theoretical Physics at Banff, Alberta, available either from the University of Alberta or from the author.

## II. “Weak Superconductivity”: The Josephson Tunneling Effect

Recently, Josephson (1) proposed that there should be a contribution to the current through an insulating barrier between two superconductors which would behave like direct tunneling of condensed pairs from one condensed gas of bound pairs at the Fermi surface to the other. Our recent observations (2) seem to confirm Josephson’s theory. Nonetheless, there are still objections in some quarters to the experiment, while in many aspects the theory is new and even uncertain. It also makes contact with interesting new aspects of many-body theory. Thus it seems worthwhile to discuss it at some length here.

The first thing it seems useful to do is to set out the bare bones of the effect before going into detail on the interesting many-body aspects of the problem. This is precisely the opposite approach to that carried out by B. D. Josephson (3) which is my major source.

We use as Hamiltonian for the problem that of Cohen *et al.* (4):

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 + \sum_{k,q} T_{kq} (C_{k\uparrow}^+ C_{q\uparrow} + C_{-q\downarrow}^+ C_{-k\downarrow}) + H.C. + \dots \quad (1)$$

$\mathcal{H}_1$  and  $\mathcal{H}_2$  are the separate Hamiltonians of the two superconductors on each side of the barrier;  $T_{kq}$  is the exponentially small tunneling matrix element from state  $k$  on one side to  $q$  on the other, and the relationship of phases shown is required by time reversal symmetry.

Prange (5) has recently made a study of Eq. (1) and concluded that it is valid from a many-particle point of view. Several interesting questions arise about this point, but as I said I am mainly concerned here with presenting the theory in simplest terms, so I will postpone discussion of this until later. I merely pause to say that Eq. (1) is a very standard form for many kinds of tunneling problems. One of many techniques for arriving at it is to find sets of single-particle functions for each side separately, in the absence of the potential of the other metal; then one eliminates the nonorthogonality effects by perturbation theory.

If the perturbation  $T$  connected states  $k$  and  $q$  within the same superconductor, we should know immediately how to deal with it. In particular, if states  $k$  and  $q$  had the same energy gap  $\Delta_k = \Delta_q$ , we would know that the energetic response to the perturbation would be identical to that of the normal metal (6, 7); while if the gaps differed in magnitude (7) or in phase, (8), the response would be lower, the energy higher.

It is necessary, on the other hand, to think more carefully about using the usual B.C.S. perturbation theory in the present case. The reason is that in a single, continuous block of superconductor it is quite correct to calculate using perfectly definite values of the *relative* phases of the energy gaps of the different states  $k$  and  $q$ , since the superconducting condensation energy actually results entirely from the precise coherence of these phases. It is however generally assumed, either because of the microcanonical assumption that the number of electrons is absolutely fixed, or because the system is in a mixed state as a result of contact with an electron reservoir undergoing fluctuations, that the total phase of the sample as a whole is meaningless. It can be shown that the state of fixed  $N$  is an average over all phase values. In fact, the total number  $N$  of pairs and the phase  $\varphi$  of  $\Delta$  are conjugate variables obeying an uncertainty relationship

$$\Delta N \Delta \varphi \lesssim 2\pi. \quad (2)$$

It is, on the other hand, not necessarily meaningless to discuss the relative phases of two blocks of superconductor which are connected by an insulating barrier sufficiently thin for tunneling to occur. Clearly, again, the total phase of the assembly as a whole is not physical, but the relative phases can be given a meaning when we observe that electrons can pass back and forth between the two through the barrier, leading to the possibility of coherence between states in which the total number of electrons is differently partitioned between the two sides—just as the phase coherence within the single block means that the number of electrons is not fixed locally and, for instance, there is coherence between the state with  $N/2$  electrons in one half of the block and  $N/2$  in the other, and that with  $(N/2) + 2$  on one side and  $(N/2) - 2$  on the other.

It thus may be meaningful to calculate the properties of the system assuming a given phase relationship. If we find—as we do—that the energy is indeed a function of the relative phase, we must presume that the phase may adjust itself in such a way as to minimize the energy, if that is possible in the presence of quantum-mechanical zero-point fluctuations or thermal fluctuations, as well as of any external stresses we may be applying which tend to break up the coherence. These aspects of the problem will be discussed exhaustively later.

Now we simply write down the standard expression for the second-

order energy perturbation caused by the transition operator in Eq. (1). A case of interest in the experiments is one in which the two energy gaps differ in magnitude so we shall maintain that degree of generality. In terms of the coherence factors  $u_k$ ,  $v_k$ ,  $u_q$  and  $v_q$  by which the Bogolyubov quasi-particles are defined,

$$\Delta E_2 = -2 \sum_{k,q} |T_{kq}|^2 \frac{|v_k u_q + v_q u_k|^2}{E_k + E_q} (1 - f_k - f_q). \quad (3)$$

Here we have allowed the energy gaps  $\Delta_k$  and  $\Delta_q$  to have arbitrary complex values, given by

$$\begin{aligned} 2u_k v_k^* &= \frac{\Delta_k}{E_k}, & 2u_q v_q^* &= \frac{\Delta_q}{E_q}, \\ |u_k|^2 - |v_k|^2 &= \frac{\varepsilon_k}{E_k}, & |u_q|^2 - |v_q|^2 &= \frac{\varepsilon_q}{E_q}, \\ E &= \sqrt{\varepsilon^2 + \Delta^2}. \end{aligned} \quad (4)$$

$E$  and  $\varepsilon$  have the usual significance, and  $f_k$  and  $f_q$  are the Fermi distribution functions of  $E_k$  and  $E_q$ . Here we have thrown away the terms with energy denominators  $\pm(E_k - E_q)$  because they are not important except near  $T_c$ .

Let us rewrite Eq. (3) using the relationships (4):

$$\Delta E_2 = -\sum_{k,q} \frac{|T_{kq}|^2 (1 - f_k - f_q)}{E_k + E_q} \left( 1 - \frac{\varepsilon_k \varepsilon_q}{E_k E_q} + \operatorname{Re} \frac{\Delta_k \Delta_q^*}{E_k E_q} \right). \quad (5)$$

This demonstrates explicitly the phase-dependent term. It will be interesting to calculate this term explicitly at the absolute zero. Let us assume  $\Delta_k$  and  $\Delta_q$  constant as functions of  $k$  and  $q$ , respectively, equal to

$$\Delta_k = \Delta_1 \exp(i\varphi_1) \quad \Delta_q = \Delta_2 \exp(i\varphi_2);$$

$\Delta_1$  and  $\Delta_2$  real; introduce the two densities of states of one spin in energy,  $N_1$  and  $N_2$ , and we obtain

$$\begin{aligned} \Delta E_2 &= -N_1 N_2 \Delta_1 \Delta_2 \langle |T_{kq}|^2 \rangle_{\text{ave}} \cos(\varphi_1 - \varphi_2) \\ &\times \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{d\varepsilon_1 d\varepsilon_2}{E_1 E_2 (E_1 + E_2)}. \end{aligned} \quad (6)$$

It will lead to negligible error to let the upper limits on the integrals tend to infinity. Then the integral is a complete elliptic integral:

$$\begin{aligned} \Delta E_2 &= -N_1 N_2 \langle |T_2| \rangle \cos(\varphi_1 - \varphi_2) \cdot \frac{4\pi \Delta_1 \Delta_2}{\Delta_1 + \Delta_2} K\left(\frac{|\Delta_1 - \Delta_2|}{|\Delta_1 + \Delta_2|}\right) \\ &\simeq -N_1 N_2 \langle |T^2| \rangle \cos(\varphi_1 - \varphi_2) \cdot 2\pi^2 \frac{\Delta_1 \Delta_2}{\Delta_1 + \Delta_2}. \end{aligned} \quad (7)$$

The last approximation is good for  $\Delta_1$  and  $\Delta_2$  not different by more than a factor 2 or 3.<sup>1</sup>

From the energy expression  $E_2$  we can easily deduce the Josephson current, as follows: in the first place, we observe that Eq. (6) is clearly not gauge invariant because it depends on the phase difference  $\varphi_1 - \varphi_2$  of the wave functions on the two sides. A gauge transformation can be performed which changes that phase, but only at the cost of changing

<sup>1</sup> The integration involves substituting first

$$E_{1,2} = \Delta_{1,2} \cosh \theta_{1,2} \quad \varepsilon_{1,2} = \Delta_{1,2} \sinh \theta_{1,2},$$

giving

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{d\theta_1 d\theta_2}{\Delta_1 \cosh \theta_1 + \Delta_2 \cosh \theta_2}$$

and then

$$u = \frac{\theta_1 + \theta_2}{2}, \quad v = \frac{\theta_1 - \theta_2}{2}$$

and

$$\cosh \theta_1 \pm \cosh \theta_2 = 2 \begin{cases} \cosh u \cosh v \\ \sinh u \sinh v \end{cases}$$

gives

$$2 \int \int_{-\infty}^{\infty} \frac{du dv}{(\Delta_1 + \Delta_2) \cosh v \cosh u + (\Delta_1 - \Delta_2) \sinh v \sinh u}.$$

The  $v$ -integration may be done trivially by the substitution  $y = e^v$ , and one gets

$$2\pi \int_{-\infty}^{\infty} \frac{du}{\sqrt{\Delta_1^2 + \Delta_2^2 + 2\Delta_1 \Delta_2 \cosh 2u}}$$

and finally this goes into a standard elliptic form by

$$\cosh 2u = x \quad \frac{dx}{2 \sqrt{x^2 - 1}} = du.$$

the vector potential  $A$ . We can deduce, assuming—as by now is permissible—that the B.C.S. theory gives gauge-invariant results, that had we calculated the energy in the presence of a vector potential  $\mathbf{A}$  we should have obtained

$$\Delta E_2 = \Delta E \cos(\varphi_1 - \varphi_2 - \frac{2e}{\hbar c} \int_1^2 \mathbf{A} \cdot d\mathbf{l}). \quad (8)$$

Here we define  $\Delta E$  as the result of the integration of Eq. (6), i.e., the coefficient of  $\cos(\varphi_1 - \varphi_2)$  in Eq. (7) or the corresponding number at finite  $T$ . We use  $2e$  in the  $A$  integration, of course, because  $\Delta$  depends on the mean value of  $\psi^* \psi^*$ , and its phase therefore transforms with the doubled charge.

Now a second general principle tells us that the current may be defined in terms of derivatives of the Hamiltonian with respect to the vector potential:

$$J = c \frac{\partial H}{\partial A}.$$

This expression is not very useful in computing ordinary transport theory currents but it can be used to calculate supercurrents. The dependence of the energy on the vector potential  $\mathbf{A}$  implies immediately the existence of a certain density of supercurrent flow:

$$\langle \mathbf{J} \rangle = c \frac{\delta \langle H \rangle}{\delta \mathbf{A}}. \quad (9)$$

In order to get mass flow per unit volume = current per unit area, we must note that  $\Delta E$  in Eq. (8) is a surface energy, and should be divided by  $w$ , the thickness of the barrier, to give volume energy. We then get

$$\langle J \rangle = \frac{2\Delta E e}{\hbar} \sin \left( \varphi_1 - \varphi_2 - \frac{2e}{\hbar c} |A| w \right), \quad (10)$$

presuming that  $\mathbf{A}$  is in the direction perpendicular to the surfaces. This then gives us for the current (again at absolute zero):

$$\begin{aligned} J &= J_1 \sin \delta\varphi \\ J_1 &= \frac{2e\Delta E}{\hbar} \cong \frac{4\pi^2 e}{\hbar} N_1 N_2 \langle T \rangle^2 \frac{\Delta_1 \Delta_2}{\Delta_1 + \Delta_2}. \end{aligned} \quad (11)$$

As remarked by Josephson, the maximum possible current is the same as the normal current at a voltage  $V_{\text{equiv}}$  equal to  $\pi \Delta_1 \Delta_2 / (\Delta_1 + \Delta_2)$  (remember that the  $\Delta$ 's are half of the "two-particle" gap). For Pb and Sn,  $\Delta_1$  and  $\Delta_2$  are approximately 1.4 mv and 0.7 mv, respectively, giving  $V_{\text{equiv}} \approx 1.5$  mv. In our best junction (2) we observed a normal resistance of  $0.4 \Omega$  giving  $J_1 = 3.75$  ma, while the actual best current was 0.65 ma. The ratio of  $\sim 6$  is quite good for critical current phenomena; it must be remembered also that our experiment was at  $\sim 1.5^\circ$  and  $J_1$  may have been as low as  $\sim 3$  ma; the temperature effect is hard to calculate and, as we shall see, other uncertainties enter.

### III. Observability and Fluctuations

Now we shall digress a little from these calculations and discuss some of the more fundamental questions of the physical aspects connected with this odd effect.

Why is it odd? The reason is twofold: that some of the predictions of the theory are unfamiliar and at first seem unphysical, and that we are very strongly conditioned against the idea of assigning a rigidly fixed value to even the relative phase angles of the wave functions on two apparently separate bits of superconductor.

The two most surprising predictions of the theory—one has been verified experimentally, the other has not—are the tiny critical field and the AC supercurrent. The former effect was my suggestion in the original Josephson letter, and arises from observing that the quantity determining the current  $J(q)$  at a given point  $y$  in the junction is not the

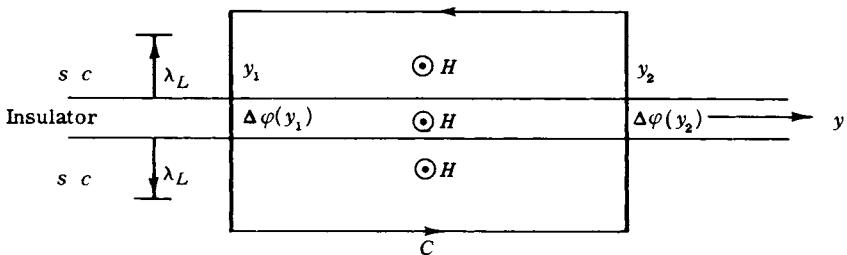


FIG. 1

phase difference  $\varphi$  between the bulk portions of the two superconductors, which is constant, but this modified for the effects of any magnetic fields which may be present in the skin layer. In particular, drawing an imaginary circuit  $c$  including legs in the two bulk regions, we see that (since we can show that  $A$  and  $j$  are negligible in the superconductors  $\perp$  to the surface)  $2\pi\Delta\varphi(y_1)$  differs from  $2\pi\Delta\varphi(y_2)$  by the ratio of the flux enclosed in the circuit to  $hc/2e$ : i. e., by the number of flux quanta enclosed. Since  $J \propto \sin \Delta\varphi$ , we will get substantial cancellation of  $J$  when  $\pi\Delta\varphi \sim \frac{1}{2}$ , i.e., when

$$2\lambda \cdot H \cdot l \sim 10^{-7} \text{ gauss cm}^2 \quad (l \text{ is the size of the junction})$$

$$\lambda \sim 5 \times 10^{-6} \text{ cm}$$

so

$$H \cdot l \sim 10^{-2} \text{ gauss cm} \quad H \sim 0.1.$$

This has been observed: we found our current doubled on reducing the field from 0.4 to 0 gauss.

It appears that the AC supercurrent is going to occur whenever we succeed in setting up an actual potential difference between the two superconductors. We can see this again in a very direct manner if we use gauge invariance. The equation of motion of the wave function  $\psi^*$  cannot involve the potential  $V$  alone or the time derivative alone, but must contain  $i\hbar(\partial/\partial t) - eV$ , so that the quantity

$$\Delta(r_1, r_2) = V(r_1, r_2) F(r_1 r_2)$$

$$F = \langle \psi^* \psi^* \rangle$$

must obey a time-dependent equation

$$\left( i\hbar \frac{\partial}{\partial t} \Delta - 2eV\Delta \right) = ( )$$

so that there must be, if there is a potential difference  $V_1 - V_2 = V$  between the two superconductors, a time dependence of the relative phase:

$$\frac{\Delta_1}{\Delta_2} = \exp(2ieVt/\hbar)$$

and so the current varies as

$$\sin \varphi \propto \sin \left( \varphi_0 + \frac{2eVt}{\hbar} \right).$$

This effect is, as far as I know, completely new to physics and represents possibly the most exciting prediction of the theory, even though the obvious practical applications do not turn out to be so very practical on closer scrutiny.

A physical way to see the origin of this current again leans on the concept of the quantum of magnetic flux: we note that each cycle of the AC corresponds to the passage through the tunnel junction of a single quantized flux line—either using

$$\frac{1}{c} \frac{d\Phi}{dt} = V \quad (\Phi \text{ the flux})$$

so that

$$\begin{aligned} \Delta\Phi/\text{cycle} &= cV(\Delta t)_{q \rightarrow q+2\pi} \\ &= \frac{cV \cdot 2\pi\hbar}{2eV} \\ &= \frac{hc}{2e}; \end{aligned}$$

or observing that the phase difference changes by  $2\pi$  each cycle, which just is the definition of a quantized flux unit.

This fact demonstrates that the AC Josephson current is really not quite a new thing under the sun. We shall see, if we find time to discuss hard superconducting wires, that in fact they can occasionally withstand a finite voltage and that, when they do, we can interpret it as the motion through them of flux quanta, which again will come through at a rate related to the voltage. Such a wire would presumably, if we could measure it, exhibit an AC supercurrent.

It is of course a well-known theorem that the phase of the wave function and the number of electrons are conjugate variables: gauge invariance, i.e., invariance under phase changes, implies number conservation in the same way that rotational invariance implies angular momentum conservation. A very simple demonstration is the following: take

a wave function with a fixed number  $N$  of particles

$$\Psi = (\psi_1^+ \psi_2^+ \dots \psi_N^+) \Psi_{\text{vac}}.$$

Multiply the field operator by a phase factor

$$\begin{aligned}\Psi' &= (e^{i\varphi} \psi_1^+) (e^{i\varphi} \psi_2^+) \dots \Psi_{\text{vac}} \\ &= e^{iN\varphi} \Psi\end{aligned}$$

and clearly  $-i \partial/\partial\varphi \Psi' = N\Psi'$

$$N \equiv -i \frac{\partial}{\partial\varphi}$$

so

$$i \frac{\partial}{\partial N} \equiv \varphi.$$

Correspondingly, there is an uncertainty principle  $\Delta N \Delta\varphi = 1$ .

Since we often work with microcanonical ensembles, and almost always with ensembles in which we superpose wave functions with different values of  $N$  only incoherently, we almost always take, either implicitly or explicitly,  $\Delta N = 0$  so  $\Delta\varphi = \infty$ : we assume the phase to be physically meaningless. In particular, in the simple example I have just given of course  $\Psi' = \text{const} \times \Psi$  so they represent the same state: a phase change is meaningless except formally. This is in fact so often the case that most physicists, until recently, have confused the concept that the phase is meaningless with the more exact statement of gauge invariance that the laws of physics are covariant under gauge transformations. Nothing prevents us from choosing to work with a state which is not gauge invariant. I think much of the psychological resistance which the B.C.S theory has encountered stems from this basic conceptual confusion.

To see the specific situation which occurs in superconductivity, let us start out with the problem of a single superconductor. A very simple way of discussing the B.C.S. theory of superconductivity is in terms of the "pseudospin" model (9-11). One does not need the full theory done that way but it is very convenient to understand the properties of certain operators from that theory. Introduce the appropriate single-electron states  $\varphi_{k\sigma}$  and the creation and destruction operators associated with them,  $c_{k\sigma}^+$ . (It is more rigorous, of course, to think of these as ac-

tually renormalized quasi-particle operators but the theory goes through either way.)

In the perfect infinite superconductor these states are states of fixed momentum and spin; in the real situation we may take them as scattered functions; in either case we introduce the precise time-reversed functions  $\varphi_{-k-\sigma} = (\varphi_{k\sigma})^*$  and their operators  $c_{-k-\sigma}^+$ . Now it is interesting to note that the sets of operators

$$1 - n_{k\sigma} - n_{-k-\sigma}$$

$$c_{k\sigma}^+ c_{-k-\sigma}^+, \quad c_{-k-\sigma} c_{k\sigma}$$

have the representation:

$$\begin{pmatrix} \sigma_z & 0 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} \frac{\sigma_x \pm i\sigma_y}{2} & 0 \\ 0 & 0 \end{pmatrix}$$

in the basis  $\left\{ \begin{array}{l} n_{k,\sigma} = n_{-k,-\sigma} = 1 \text{ or } 0 \\ |n_{k\sigma} - n_{-k-\sigma}| = 1 \end{array} \right.$

Thus these have the algebraic properties of a spinor: let us call them  $\sigma_{kz}, \sigma_k^\pm$ .

Now form the operators

$$S_z = \sum_k \sigma_{kz} \quad S_x, S_y = \sum_k \sigma_{kx}, \sigma_{ky}$$

$$= \text{const} - N_{\text{total}}$$

The most basic characterization of the B.C.S. state is that the operators  $S_x$  and  $S_y$  have macroscopic values in it. In a state of fixed  $N$  — i.e., fixed  $S_z$  — in view of the commutation relations  $\mathbf{S} \times \mathbf{S} = i\mathbf{S}$ ,  $S_x$  and  $S_y$  cannot have definite values; in such a state they can have large off-diagonal matrix elements. In the simple product state,

$$\prod_k (\sqrt{h_k} + \sqrt{1-h_k} c_k^+ c_{-k}^+) \Psi_{\text{vac}}.$$

$S_x$  does have the large value

$$\sum_k \sqrt{h_k(1-h_k)}.$$

By inserting a factor  $e^{i\varphi}$  in  $\sqrt{1 - h_k}$ , we may rotate this large value around the  $z$  axis to any desired location; in this case, because  $N$  is not fixed these wave functions are physically distinct but, of course, all must have the same energy.

We can project out a state of fixed  $N$  by the subterfuge:

$$\Psi_N = \int \exp [-i(N/2)\varphi] \prod_k (\sqrt{h_k} + \sqrt{1 - h_k} e^{i\varphi} c_k^+ c_{-k}^-) \Psi_0 d\varphi.$$

This is equivalent to the transformation coefficient  $\exp(ipq)$  between  $p$  and  $q$  representations.

In the isolated superconductor, no particular gain is made by using either  $N$  or  $\varphi$  representations. In fact, however, the  $N$  representation is correct, because there is actually a term in the energy depending on  $N$ , namely the electrostatic energy. Even if we prepared the superconductor in the product-type state, this state would dissipate like a wave packet of free particles because of the energy  $[e^2(N - N_0)^2]/2C$ , where  $C$  is the electrostatic capacity  $\sim 1$  cm. The "kinetic" energy, then, of a state with an uncertainty of  $\varphi$  of  $\sim 1$  would be of order  $(e^2/C) \langle (\partial/\partial\varphi)^2 \rangle$

$$\sim \frac{25 \times 10^{-20}}{1} \sim 10^{-18} \text{ ev}$$

and the corresponding time for the "packet" to dissipate would be  $10^{-9}$  sec. Thus, in fact, real superconductors cannot be prepared, in isolation, in states with coherent superpositions of different  $N$  values: the common assumption that  $N$  is fixed,  $\varphi$  meaningless is correct.

The opposite situation precisely is the case when we consider different parts of the same superconductor, their relative phase and number relationship. Clearly we can define for individual superconductors, or different pieces of the same superconductor, relative variables  $n = N_1 - N_2$  and  $\varphi = \varphi_1 - \varphi_2$ , and again

$$n = -i \frac{\partial}{\partial\varphi} \quad \varphi = i \frac{\partial}{\partial n}$$

For two different parts of the same superconductor, the very experimental facts about the Meissner effect, persistent currents, etc., tell us that the relative  $\varphi$  is fixed rigidly and therefore the state must be one in which

locally there is coherent superposition of different  $n$  states:  $\varphi$  is fixed so  $n$  is uncertain. The existence of persistent ring currents tells us that the gap  $\Delta$ —which is equivalent to  $S_{\text{transverse}}(r)$  or to  $\Psi'$  in Landau-Ginzberg—is strongly constrained to be single-valued and continuous throughout an entire macroscopic sample.

It is clear that there must be a dividing line between these two behaviors, perfect phase coherence and negligible coherence. This is the Josephson effect.

The most straightforward situation we might study is the following: two superconductors separated by a barrier and left on open circuit. We also ignore radiation for now: actually probably very little power

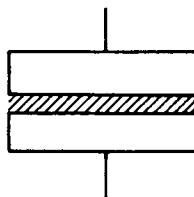


FIG. 2

can be radiated because of the thinness of the barrier layer. The trivial theory tells us that that part of the energy which depends on the phase difference operator is

$$E_1(1 - \cos \varphi)$$

A second term in the energy is the electrostatic energy associated with any difference in charge between the two sides. This of course is just

$$\frac{Q^2}{2C} = \frac{e^2(n^2)}{2C}$$

so that the total Hamiltonian is just precisely that of a pendulum:

$$H = \frac{e^2}{2C} n^2 + E_1(1 - \cos \varphi)$$

where  $[n, \varphi] = 1$ , so that  $n$  plays the role of the momentum,  $\varphi$  that of the coordinate.

Now the relevant question is just whether the thermal or zero-point fluctuations of the energy are or are not outweighed by the coupling  $E_1$  which tends to keep the phases of the energy gaps on the two sides coupled.

The zero-point energy is usually negligible. If we approximate the lower part of the cosine curve by a parabola, we get a harmonic oscillator of frequency

$$\hbar\omega = \sqrt{\frac{e^3}{C} E_1} \quad \frac{\hbar\omega}{E_1} = \sqrt{\frac{e^2}{CE_1}}.$$

Usable junctions have thicknesses  $\sim 10^{-6}$ - $10^{-7}$  cm, and areas  $\sim 10^{-2}$ - $10^{-3}$  cm, so  $C \sim 10^4$  cm; thus  $E_1 = 25 \times 10^{-20}/10^4 \sim 10^{-22} = 10^{-10}$  ev is the point at which zero-point energy will destroy coherence. This corresponds to a total current of the order  $10^{-13}$  amp. This is unmeasurable but corresponds actually to a film not excessively thick — 100 Å of good insulator would probably effectively decouple two superconductors. Nonetheless, the zero-point kinetic energy is quite small, corresponding to a large effective “mass.”

Much more important is obviously the purely classical effect of thermal fluctuations, which will clearly be of importance whenever  $kT \sim E_1$ . A current  $J_1$  of  $10^{-3}$  amp corresponds to an  $E_1$  of  $\hbar J/e$  where  $J$  is in esu  $\sim 3 \times 10^6$

$$E_1 = \frac{10^{-27} \times 3 \times 10^6}{5 \times 10^{-10}} \sim \frac{3 \times 10^{-11}}{5} \sim 5 \text{ ev.}$$

This should be reasonably stable against room temperature thermal fluctuations, but  $J_1$ 's of  $10^{-4}$ - $10^{-5}$  amp will in most measuring apparatus be thermally uncoupled.

We can also see something from this isolated and simple system about what will happen at finite voltages. If we were to charge up the condenser to some value  $Q = en$ , we would put our pendulum-like system into a state corresponding to rotation of the pendulum about the fulcrum. Classically, we have given the system an effective average “momentum”  $n$ , and

$$\frac{d\varphi}{dt} = \frac{1}{\hbar} \frac{\partial H}{\partial n} = \frac{1}{\hbar} \frac{e^2}{c} n_{\text{ave}} = \frac{eV_{\text{ave}}}{\hbar}.$$

Thus the phase rotates at the average velocity  $eV$  (the correct charge to use in this equation is of course two electronic charges).

At the same time,  $n$  will not — again classically — remain absolutely constant: it will have a value

$$n = -\frac{\partial H}{\hbar \partial \varphi} = -\frac{E_1}{\hbar} \sin \varphi(t)$$

so that

$$Q = J = J_1 \sin \varphi(t) :$$

we find an alternating current at the average frequency  $2eV/h$ . This is the original Josephson current term.

Quantum mechanically, this phenomenon will look somewhat different: the frequency will correspond to an energy-level difference, the current to a large off-diagonal matrix element of the electromagnetic interaction; but in view of the fact that the quantum zero-point energy is so terribly small relative to the thermal fluctuations, because of the large capacity, the classical theory of our effective “pendulum” is certainly adequate.

Whether this AC effect is measurable depends on a number of factors, some of which I understand and some of which, undoubtedly, I do not. One difficulty is the intrinsic smallness of the effect. The large capacity of the barrier layer — or at least a very low impedance — seems to be an inescapable difficulty. As we computed, this capacity is of the order  $10^4$ - $10^5$  esu, or  $10^{-2}$ - $10^{-1}$  microfarad. The frequency  $\omega$  is  $\sim 10^{18} V_{\text{esu}}$  or  $3 \times 10^{15} V_{\text{volts}}$ , so that a small voltage of the order of  $10^{-4}$  volts, a tenth of the gap, would lead to a frequency  $\omega$  of  $3 \times 10^{11}$  cps, at which the impedance  $Z$  of the barrier would be only  $10^{-4}$  ohms, the alternating voltage only  $0.1 \mu\text{volt}$ , and the available energy/second only  $C\omega V^2 \sim 10^{-10}$  watt.

We might try to achieve a smaller voltage and frequency, at which all of these figures would be improved, but actually we have at most only an order of magnitude available, because the AC regime necessarily requires that the electrostatic energy be large in comparison to  $E_1$ , which occurs at about  $C(V_{\text{esu}})^2 = E_1 \sim 10^{-11}$  erg

$$V_{\text{esu}} \sim 10^{-8}, \quad V = 3 \mu\text{volts}.$$

This is also — obviously — the point at which the AC voltage becomes

comparable with the DC, so that the junction is capable of putting *itself* back into the pure DC regime.

Thus it appears unlikely that frequencies less than 10 kilomegacycles can be seen, while above this point serious amplitude problems are evident.

An additional difficulty which may not be widely enough appreciated is that of noise. In an actual circuit the voltage, and therefore the frequency, will be subject to severe thermal fluctuation. In the DC situation the fluctuations can be ignored, once the coupling  $E_1$  is considerably greater than  $kT_{\text{circuit}}$ , because the coupled state is the thermal equilibrium one. In the AC situation, however, we are forcing the system to be in a state above its equilibrium one, and there is nothing preventing fluctuations from occurring. A rough estimate based on noise power in the circuit of  $kT$  per unit bandwidth leads to an estimate of the frequency fluctuation bandwidth of

$$\Delta\omega \sim \sqrt{\frac{kT}{\hbar}} \cdot \frac{e^2}{\hbar c} \sim \sqrt{10^{13} \cdot 10^4} \sim 3 \times 10^8 \text{ cps.}$$

Again, obviously we are forced to work only at high frequencies.

Perhaps the best scheme for observing the effect is that of Josephson, which does not seem to run aground on fluctuation effects. This is the idea of synchronizing with an externally applied AC field and current. This synchronization must, again, be achieved against a background of thermal fluctuations. Thus we must have the Josephson current to external voltage coupling  $\gg kT$  to get a large effect. With the total AC charge only of the order  $\Delta Q \sim J/\omega \sim 10^{-15}$  coulomb, this requires  $V \sim 1 \mu\text{volt}$ , and a current of order  $10^{-2}$  amp: a power requirement which does not seem excessive.

All this is rather speculative, however; the AC effect has not been observed, and the circuit problems as well as any possible additional physical effects are as yet unknown territory. I believe that the DC, zero voltage Josephson effect has been observed, and I will give here a brief discussion of it.

What is observed, of course, is not the phase coupling directly but the fact that the system can pass a DC current in the absence of voltage, just like an ordinary superconductor. In fact, many things about the mechanism of this effect are very closely analogous to ordinary super-

conductivity: that is why I think a good synonym for it is “weak superconductivity.”

The isolated pair of superconductors cannot pass a current; thus we must add to the system a current generator. In actual experiments, of course, this usually consists of a voltage source with a high resistor in series; but it is simpler to add to our energy expression a term for a current source, given by

$$\frac{\partial E_{\text{source}}}{\hbar \partial \varphi} = \dot{n} = -\frac{J_{\text{ext}}}{2e}$$

$$E_{\text{source}} = -\frac{\hbar J_{\text{ext}}}{2e} \varphi.$$

Thus the potential energy as a function of  $\varphi$  now takes the form

$$E = E_1(1 - \cos \varphi) - \frac{\hbar J_{\text{ext}}}{2e} \varphi$$

and equilibrium occurs at

$$\begin{aligned} \frac{\partial E}{\partial \varphi} = 0 ; \quad E_1 \sin \varphi &= \frac{\hbar}{2e} J_{\text{ext}} \\ J_{\text{int}} = J_{\text{ext}} &= \frac{2eE_1 \sin \varphi}{\hbar}. \end{aligned}$$

Thus a current flows, and can flow up to  $J = J_1$ , at least in classical theory and at absolute zero.

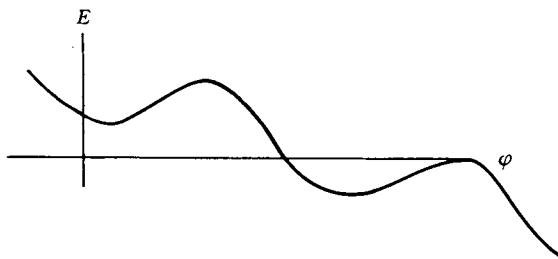


FIG. 3

Two effects act to limit the amount of DC current that can flow: thermal fluctuations and the presence of magnetic fields. As we explained earlier, the coupling fails unless  $E_1 \gg kT$ ; we can see that in the presence

of the "tilted" energy corresponding to a current generator, thermal activation could allow our system to hop from one valley to the next, leading to a finite  $\varphi$  and therefore an externally visible voltage.

Both externally applied magnetic fields and those caused by the current itself can reduce drastically the current-carrying capacity of a Josephson junction. We explained previously the effect of external fields; we can think of this as introducing a distribution in phase over the sinusoidal  $E_1(1 - \cos \varphi)$  curve, which effectively reduces the activation barriers. Internal fields will do the same if the size of the junction is greater than an effective "penetration depth"

$$\lambda_{\text{eff}} = \left( \frac{16\pi J_1 e \lambda_L}{\hbar c} \right)^{-1/2}$$

$\lambda_L$  being the average London penetration depth in the superconducting material. This is typically  $\sim 0.01$  cm.

Pippard (12) has pointed out that the external field effect should be periodic as well as decaying. Confirmation of this would do much to verify the theory.

When the effect was first predicted, the most serious problem about it seemed to be the fact that it had never been seen, although thousands of junctions had been measured experimentally. We now believe that the main reasons are threefold: most important, the fact that junctions which are easy to measure in the gap region are of normal resistance  $\sim 100 \Omega$ , so that  $E_1$  was not large enough relative to  $kT$ . Second, the field effect: no one previously had measured in the absence of the earth's field. Finally, it is easy to ascribe the effect if seen to tiny superconducting shorts, and only quantitative investigation distinguishes it. Most important of the proofs against superconducting shorts is the field effect. As in filamentary superconductors, one would expect the flux quanta to go through the insulating spaces between the shorts, leaving the shorts superconducting. But that would lead to high critical fields. It is also to be noted that sufficiently finely divided systems of very small shorts will themselves be Josephson tunnels: after all, even in the oxide there are rows of metal ions, but we do not consider these to be shorts.

#### IV. Connection to General Many-Body Theory of Condensed States and "Broken Symmetry"

In general, a condensation phenomenon is characterized by the appearance of a new parameter in what we call the "condensed" phase which was not present in the original system. For example, below its Curie point a ferromagnet has magnetization in the absence of a field. The long-range order of a solid is not present in the liquid; the antiferromagnet and order-disorder have less evident but still easily measurable "order parameters." In the ferroelectric it is the electric moment. More elusive is the liquid-gas system, in which we must think of the order parameter as the difference in behavior of the two phases. The order parameter of the superconductor is the energy gap itself.

All of these systems and their order parameters have a very important feature in common: that the system with fixed order parameter has a much lower degree of symmetry than the uncondensed system. We can state it this way: the condensed system does not have the full symmetry of the Hamiltonian of which it represents a statistical solution. In each of the above examples we see this exemplified. The ferromagnet does not have the full symmetry of spin rotation of the spin Hamiltonian; even more seriously, it does not have time-reversal invariance. The ferroelectric does not have space-inversion invariance. The solid is presumably a solution of a Hamiltonian with full translational as well as rotational invariance, yet we commonly think of it as being a rigid lattice rigidly fixed in space, translationally as well as rotationally. The other examples can be shown to agree with this idea, except for superconductivity and superfluidity, which are rather different. Superfluidity is very similar to superconductivity, so we shall concentrate on the latter. We can subsume superconductivity under the general theory if we let the order parameter be  $\Delta$  and fix  $\Delta$  in phase as well as amplitude. Then it is gauge invariance, in a certain sense, which is violated in the superconductor. Of course, general gauge invariance is not violated, but from the point of view of individual electrons it is, in the sense that the phase of the field operator with which we insert additional particles is physically relevant.

It is, of course, physically obvious that the full symmetry of the original Hamiltonian still governs the system, in the sense that it is only

the state of the system which is taken to be noninvariant, and one considers all other states to which the assumed state can be carried by symmetry operations as degenerate with the given one. In ferromagnetism, we assume the various possible magnetized states to be equal in energy, or at least — in the presence of crystal anisotropy — the state and its time reversal. We assume, in the absence of external forces, that all positions and orientations of a crystalline solid are degenerate, that a ferroelectric may be polarized in at least two crystalline directions, or in fact that the phase of the energy gap in the superconductor is arbitrary, and the energy independent of it.

These ideas so far seem perfectly self-evident and general. Now, however, we come to a real distinction among the various cases. In a few case — ferromagnetism being the only obvious example — the order parameter is a rigorous constant of the motion, or nearly enough so for any usual purposes. Then, of course, the noninvariant states are, nonetheless, rigorous, degenerate eigenstates of  $H$ , and no serious questions of principle arise: all the consequences of the true symmetry of  $H$  can be retained in the most naïve fashion.

Much more common is the opposite case: the order parameter is not a quantum mechanical constant of the motion. The orientation of the solid in space, for instance, or its position, are not constants of the motion; the correct constants are total momentum and angular momentum. A very similar situation occurs in antiferromagnetism, which was I believe the first case in which these phenomena were carefully elucidated (13). Finally, in the superconductor we find the phase variable not just not a constant of the motion, but normally assumed to be meaningless.

In these cases one finds that condensation has much more interesting consequences in principle. Certain apparently obvious symmetry theorems cannot be retained any more: a nice example is the famous theorem that a system can have no electric dipole moment, which is certainly badly violated in a ferroelectric.

In the cases of the solid, the antiferromagnet, or the ferroelectric, we can understand very well the physics of the situation. What happens is that the condensation has given the system one form or another of long-range order, so that the  $\sim 10^{23}$  different atoms must move as a unit rather than individually. Under these circumstances the system is so

large that its behavior is essentially classical, and we may fix the value of the order parameter even though it is not a constant of the motion — the coordinate or orientation of the solid, for instance. There is indeed a zero-point motion of a macroscopic solid, but it is so small that we needn't concern ourselves with it.

Another aspect of the situation is that in general the usual type of condensed system finds itself in the presence of external forces which fix the order parameter at some definite preferred value. Because of the long-range order, only a very small external force is necessary to do this. A small external field can align a ferromagnet, a small external force pin down the orientation and position of a crystal.

In actual fact we seldom deal with condensed systems in the absence of external forces, so that we are accustomed to think of such systems as having definite values of such order parameters as the orientation. But this is because we are accustomed to working with measuring instruments which are themselves macroscopic condensed bodies: in the case of solids, with measuring instruments which are themselves rigid i.e., have long-range positional order. Thus it does not seem extraordinary to us that a solid has fixed position and orientation. In the case of magnets, again we are used to instruments which violate time-reversal symmetry themselves — through the second law, for one thing — and so we do not find it very extraordinary for a system to have a definite value of ferro- or antiferromagnetic order.

In the case of superconductivity things are quite different. The internal long-range order parameter — the phase — is not a parameter for which suitable instruments exist; we do not normally walk around with objects which have phase order. A superconductor has rather perfect internal phase order, but as we have shown the zero-point motion of the total order parameter of an isolated superconductor is large and rather rapid.

The importance of the Josephson effect, then, is that it provides for the first time an instrument which can act like a clamp for a solid or a coercive field for a ferromagnet: it can pin down the order parameter, allow a basis for intercomparisons, etc. But most important of all, it frees us conceptually from the mystery surrounding superconductivity, and places it in line with all of the other condensation phenomena.

To summarize: In each case, condensation is a self-consistent choice

by the system of a state — and a corresponding mean self-consistent field — which does not have the full symmetry of the Hamiltonian. In each case, this choice must be made consistently throughout macroscopic volumes of the sample, because a relatively large coupling energy maintains this. But in almost every case, we can expect quantum fluctuations of the order parameter which will, in the absence of unsymmetric external forces, restore the full consequences of the original symmetry. The external forces necessary to “pin down” the quantum fluctuations can only come from systems which themselves violate the given symmetry. This then is the importance of Josephson’s weak superconductivity: it is the only coupling force playing this role for a superfluid.

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# Tunneling from a Many-Particle Point of View<sup>1</sup>

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In this book are mentioned a number of applications of the theory of tunneling, and there are numerous others, ranging from nuclear pickup processes to the Esaki diode. However, we shall keep in mind, metal-to-metal tunneling through an oxide layer. In the courses in quantum mechanics which we had in our youth, we solved the problem of the tunneling of a single electron. This we did by considering an incident wave, a reflected wave, and a transmitted wave. The transmission coefficient can be calculated in some approximation (usually the WKB approximation). As is well known, the transmission coefficient depends chiefly upon an exponential factor

$$\exp \left[ -2 \int_{x_0}^{x_1} \varkappa(x) dx \right]$$

where  $\varkappa(x)$  is  $\sqrt{2m [V(x) - \varepsilon_k]}$ . Here we have already adopted the potential barrier model of the tunneling junction, and the WKB approximation, but the main features of this result are certainly of more general validity. However, we shall not discuss the calculation of the transmission coefficient further, because we are interested here in many-particle effects. Besides, most of the time, the experimenter has no independent measure of the thickness of the barrier, which usually is a horrible mess.

The simplest model of the metal system is that of independent quasi particles, in which we take into account only the Pauli principle. The results for this model can be obtained easily if we know the individual

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transmission coefficients. We have to make sure that there is an empty state available into which the electron tunnels, so that at zero temperature, for example, we can have a current only when we have applied a potential difference across the barrier. The effect of interaction in this case is obscured. However, for most purposes, this model provides excellent framework within which one can understand experimental results.

Recently, Bardeen (*I*) pointed out that it was superior to recognize the smallness of the parameter  $|T|^2$ , the tunneling coefficient, at the outset. Instead of treating the tunneling as a sort of scattering process, he treated it as a transition process between nearly stationary states.

Let  $\Phi_0$  be the state at the initial time. In the absence of any tunneling, this state will evolve in time according to  $\Phi_0(t) = \Phi_0 \exp(-iE_0 t)$ . However, if one allows tunneling, the state will evolve into  $\Psi(t) = \Psi_0(t) + \sum_v a_v(t) \Phi_v \exp(-iE_v t)$ . The  $\Phi_v$  are states in which an electron has passed across the barrier. We remark that  $(\Phi_v, \Phi_0) \neq 0$ , but this sort of expansion is well understood. Let us apply time-dependent perturbation theory. We calculate

$$\begin{aligned} \left( i \frac{\partial}{\partial t} - H \right) \Psi(t) &= (E_0 - H) \Phi_0 \exp(-iE_0 t) \\ &\quad + \sum_v i a_v(t) \Phi_v \exp(-iE_v t) \\ &\quad + \sum_v a_v(E_v - H) \Phi_v \exp(-iE_v t) = 0. \end{aligned}$$

Thus

$$i \frac{\partial}{\partial t} a_v = (\Phi_v, (H - E_0) \Phi_0) \exp[-i(E_0 - E_v)t].$$

Then,

$$\frac{d}{dt} |a_v(t)|^2 = 2\pi |(\Phi_v, (H - E_0) \Phi_0)|^2 \delta(E_0 - E_v). \quad (1)$$

This is the rate at which the initial state is transformed into the state  $\Phi_v$ . Bardeen has shown how one can rewrite the matrix element above in a more natural form. Consider the  $x$ -coordinate (perpendicular to the barrier) of the electron which has tunneled. Call the midpoint of the barrier  $x = 0$ . Then, for positive  $x$ , say  $\Phi_0$  is practically an eigenstate of  $H$ , so we may write

$$\begin{aligned}
 (\Phi_r, (H - E_0)\Phi_0) &= \int \dots \int^0 dx [\Phi_r^* (H - E_0) \Phi_0(x_1 \dots x \dots)] \\
 &= \int \dots \int^0 dx [\Phi_r^* (H - E_0) \Phi_0 - \Phi_0 (H - E_r) \Phi_r^*]
 \end{aligned}$$

since the second term vanishes for negative  $x$ . Since  $E_r = E_0$  we have

$$\begin{aligned}
 (\Phi_r (H - E_0) \Phi_0) &= \int \dots \int^0 dx \left( -\frac{1}{2m} \frac{\partial}{\partial x} \right) \left( \Phi_r^* \frac{\partial}{\partial x} \Phi_0 - \Phi_0 \frac{\partial}{\partial x} \Phi_r^* \right) \\
 &= -i[J_x(0)]_{r0}. \tag{2}
 \end{aligned}$$

Here  $J_x(0)$  is the operator for the total current passing across the plane  $x = 0$ .

This is Bardeen's calculation, with which it is hardly possible to quarrel. Various people (2-4) have immediately jumped to the conclusion that it should be possible to represent the Hamiltonian in the presence of the barrier by

$$H = H_R + H_L + T + \dots \tag{3}$$

where

$$T = \sum_{m,n} T_{mn} a_m^\dagger b_n + \text{Hermitian conjugate.}$$

Here  $a_m^\dagger$  creates electrons in a state on the right and  $b_m^\dagger$  creates electrons on the left. The labels  $m, n$  refer to some set of single particle states, not necessarily plane waves. The dots refer to terms of order  $T^2$  and smaller. It is also assumed that  $T_{mn}$  does not depend on interaction to any appreciable degree.

This is also a conclusion which we do not wish to dispute. However, it might be valuable to examine in some model, in exactly what sense Eq. (3) is correct.

In the following, I shall describe the contents of a note of my own (5).

Let us adopt the single model of a tunnel junction described by a potential  $V(x)$  (Fig. 1).

It is hard to believe that the symmetry, the simple barrier, or the specular nature of the transmission will change the results much, but I certainly have not examined in detail what errors these simplifications

may have introduced. If we stick to this model then, the Hamiltonian is

$$H = H_0 + V + W \quad (4)$$

where  $H_0$  is the independent electron Hamiltonian,  $V(x)$  is graphed in Fig. 1, and  $W$  is the interaction between electrons, or between electrons and phonons.  $H_0$  does not have to be the free-electron Hamiltonian.

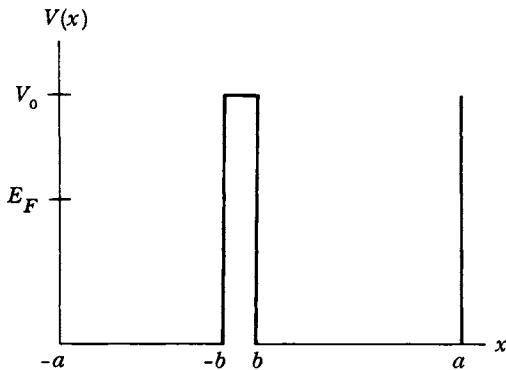


FIG. 1

The problem we wish to solve is this: Express the  $H$  of Eq. (4) in the form of Eq. (3). To solve this problem we have to decide what the labels  $m, n$  appearing in Eq. (3) really mean. What we would *really* like heuristically is to express the annihilation operator  $\psi(x)$  as

$$\psi(x) = \sum_m \varphi_m'(x)a_m + \chi_m'(x)b_m \quad (5)$$

where (a) the  $\varphi'$ , and  $\chi'$  together form a complete orthonormal set, (b) any electron confined to the right (left) of the barrier can be expressed solely in terms of the states  $\varphi_n'(\chi_m')$ , (c) the single-electron Hamiltonian is a well-defined operator on all  $\varphi', \chi'$  functions.

If we had such states, life would be simple, since we could substitute Eq. (5) into (the second quantized form of) Eq. (4), segregate the  $a$  and  $b$  operators into  $H_R$  and  $H_L$ , and what is left over would be  $T$ .

This explains why we need assumption (c) above, since without it, the substitution of (5) into (4) is not possible, or at best it is tricky. In fact, one does not want to deal with states  $\varphi'$ ,  $\chi'$ , which involve single-particle energies which are too great, otherwise  $H_R$ , for example, is too unlike the barrierless Hamiltonian we want. It is unfortunate, because states which vanish identically for one or the other sign of  $x$  are thereby ruled out and in consequence, we cannot satisfy both assumptions (a) and (b).

Since we have to give up one of these two assumptions, let us examine which one we should give up. I want to argue that assumption (a) must be foregone, at least the part which says "orthonormal."

I have not worked out a formal proof, but it appears to be true that complete orthonormal sets which do not involve high single-particle energies always have this condition: although they can be more or less confined to one side of the barrier, there is a long tail which leaks through. This tail is not negligible, because it really describes the effect which is under study. If we inject an electron into the right side of the tunnel junction, the tunneling rate is just given by the amount of "left-hand" wave function which is needed to form the initial wave packet.

An example of this state of affairs is shown in our model. The single particle eigenstates are even or odd in  $x$ . A complete orthonormal set is therefore

$$\Phi_k'[x_k'] = 2^{-1/2} [e_k(x) \pm o_k(x)]$$

where  $e_k(o_k)$  are the even (odd) eigenstates of  $H_0 + V$ . However,

$$\frac{d}{dt} N_R = i \left\langle \left[ \sum_k a_k^+ a_k, H \right] \right\rangle$$

is not constant for small times, as we expect on physical grounds. Instead,  $N_R$  oscillates in time, a behavior which is well known in elementary quantum mechanics, but is not observed in tunnel junctions.

The way out is to introduce  $c_n$  and  $d_n$  operators, (so no confusion arises with  $a_n$  and  $b_n$ ), where

$$\psi(x) = \sum_n c_n \varphi_n(x) = \sum_n d_n \chi_n(x). \quad (6)$$

In the symmetrical model, we may take  $\varphi_n(x) = \chi_n(-x)$  and we suppose they satisfy, say,

$$[H_0 + V_1(x)] \Phi_n(x) = \varepsilon_n \varphi_n(x)$$

where  $V_1(x)$  is graphed in Fig. 2.

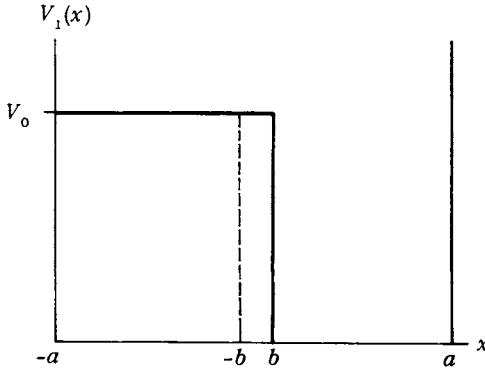


FIG. 2

The only important feature is that we somehow keep the leakage through the barrier of  $\varphi, \chi$  to a minimum. Both  $\{\varphi_n\}, \{\chi_n\}$  are complete orthonormal sets. We want to express the Hamiltonian in terms of the  $c$ 's and  $d$ 's, as before, but in such a way that we do not mix up the single-particle energies more than is necessary. (This additional condition is necessary, because we have two orthonormal complete sets to do the job of one.)

The prescription is simple and obvious for the symmetrical case. I have never worked it out in general, but I do not doubt it can be done. The recipe is this: Express  $H$  in terms of the even and odd states  $e_k(x)$ ,  $o_k(x)$ . Express these in turn according to

$$\begin{aligned} e_k(x) &= \sum_n [\varphi_n(x) + \chi_n(x)] \lambda_{nk} \\ o_k(x) &= \sum_n [\varphi_n(x) - \chi_n(x)] \mu_{nk}. \end{aligned} \tag{8}$$

It is completely straightforward, even if a little tedious, to evaluate

the expansion coefficients  $\lambda, \mu$ . The result is

$$\begin{aligned}\lambda_{kl} &= 2^{-1/2} [\delta_{kl} - T_{kk}/(\varepsilon_k - \varepsilon_l) - \frac{1}{2} \xi_{kl} + \dots] \\ \mu_{kl} &= 2^{-1/2} [\delta_{kl} + T_{kk}/(\varepsilon_k - \varepsilon_l) + \frac{1}{2} \xi_{kl} + \dots].\end{aligned}\quad (9)$$

We have introduced the single-particle matrix element of the current-across-the-barrier operator of Bardeen. Since we will always be interested in situations for which  $\varepsilon_k$  does not differ too much from  $\varepsilon_l$ , we can just keep the diagonal element. For these situations,  $\xi_{kl}$  is given by the overlap

$$\xi_{kl} = (\varphi_k, \chi_l)$$

and vanishes for states differing largely in energy (even though the inner product does not).

Perhaps for completeness it can be recorded that

$$T_{kl} = \delta_{kyly} \delta_{kziz} \frac{2\alpha \exp(-2\alpha b)}{ma[1 + (\alpha/k)^2]}$$

where  $\alpha$  was defined before, and  $k_x$  is the wave number in the  $x$  direction. In this model,  $T_{kl}$  is diagonal, except for the variable  $k_x$ .

Neglecting, for now, the interaction, we have

$$\begin{aligned}H &= \sum_{klm} (\varepsilon_k^{(\text{even})}) \lambda_{ki} (c_l^\dagger + d_l^\dagger) \lambda_{im} (c_m + d_m) \\ &\quad + (\varepsilon_k^{(\text{odd})}) \mu_{kl} (c_l^\dagger - d_l^\dagger) \mu_{km} (c_m - d_m)\end{aligned}$$

where

$$\varepsilon_k^{(\text{even})} \cong \varepsilon_k - T_{kk}$$

$$\varepsilon_k^{(\text{odd})} \cong \varepsilon_k + T_{kk}.$$

The algebra can be done easily, with the result

$$\begin{aligned}H &= \sum_k \varepsilon_k c_k^\dagger c_k + \sum_k \varepsilon_k d_k^\dagger d_k \\ &\quad - T_{kl} (c_k^\dagger d_l + d_l^\dagger c_k) \\ &\quad - \frac{1}{2} \xi_{kl} (\varepsilon_k + \varepsilon_l) (c_k^\dagger d_l + d_l^\dagger c_k) + \dots\end{aligned}\quad (10)$$

This is what we expected, except for the last term (in  $\xi_{kl}$ ). However, we should not forget that the  $c_k^\dagger$  do not commute with the  $d_l$ , but that

$$\{c_k^\dagger, d_l\} = \xi_{kl}.$$

Therefore,  $H_R = \sum_k \varepsilon_k c_k^\dagger c_k$  does not commute with  $H_L = \sum_k \varepsilon_k d_k^\dagger d_k$ . Consider, however, the effect of  $H_R + H_L$  on some product state,

$$\Phi_R \Phi_L |0\rangle$$

where  $\Phi_R$  contains only  $c^\dagger$ 's, and  $\Phi_L$  contains only  $d^\dagger$ 's. Then

$$\begin{aligned} (H_R + H_L) \Phi_R \Phi_L |0\rangle &\simeq \Phi_L H_R \Phi_R |0\rangle \\ &+ \Phi_R H_L \Phi_L |0\rangle \\ &+ \sum_{kl} \varepsilon_k \xi_{kl} (c_k^\dagger d_l + d_k^\dagger c_l) \Phi_R \Phi_L |0\rangle. \end{aligned} \tag{11}$$

Thus, for processes such that  $\varepsilon_k \sim \varepsilon_l$ , the  $H_R$  may be regarded as commuting with  $H_L$ , provided we at the same time drop the last term of Eq. (10), which we wanted to do anyway.

The remaining thing is to consider the effects of interactions on this formulation. Suppose, for example, we have an electron-phonon interaction. We can write this as

$$H_{lp} = \sum_q \nu_q^i Q_q \varrho_q$$

as discussed by Professor Pines in this volume.  $Q_q$  is the canonical coordinate of the phonon, and  $\varrho_q$  is the density operator,

$$\varrho_q = \int \psi^\dagger(x) \psi(x) \exp(iq \cdot x) d^3x. \tag{12}$$

We want to express the  $\psi(x)$  in terms of the localized operators  $c_n$  and  $d_n$  as before.

This may be done, with the result

$$\varrho_q \approx \sum_{mn} \varrho_{mn}^{qa} c_m^\dagger c_n + \varrho_{mn}^{la} d_m^\dagger d_n + \varrho_{mnq}^T (c_m^\dagger d_n + d_n^\dagger c_m). \tag{13}$$

We have written

$$\varrho_{mn}^{rq} = \int \varphi_m \varphi_n \exp(iq \cdot x d^3x)$$

$$\varrho_{mn}^{lq} = \int \chi_m \chi_n \exp(iq \cdot x d^3x)$$

which just represent the usual electron-phonon interaction in the main part of the metal. (We have tacitly ignored the effect of the barrier on the phonons which, if taken into account, would complicate the formula.)

The amplitude  $\varrho_{mnq}^T$  is expressed by

$$\begin{aligned} \varrho_{mnq}^T &= \int \varphi_m \chi_n \exp(iq \cdot x d^3x) \\ &- \sum_s \xi_{ms} \varrho_{sn}^{lq} - \xi_{ns} \varrho_{ms}^{rq}. \end{aligned} \quad (14)$$

We should not forget, however, that the  $c$ 's and  $d$ 's do not quite commute. We can pretend that they do, however, provided we drop the last terms (in  $\xi_{rs}$ ) in Eq. (14).

Thus, the effect of the interaction on the tunneling is expressed by the addition of the small term

$$\sum v_q i Q_q \varrho_{mn}^{qc} (c_m^\dagger d_n + d_n^\dagger c_m) \quad (15)$$

to the Hamiltonian, where

$$\varrho_{mn}^{qc} = \int \varphi_m \chi_n \exp(iq \cdot x) d^3x. \quad (16)$$

This is rather small, not only because it involves the overlap of the  $\varphi$ ,  $\chi$  functions, but because their overlap is rather smooth (in the  $x$  direction) over a region of (say) 30 Å. Thus, if  $q_x$  is not too small, we can expect this factor to be small. However, I don't believe it has been taken into account in the discussion of Kadanoff and Schrieffer in this volume.

In summary, it can be said that insofar as the simple model we have adopted has not led us seriously astray, it is possible to write the Hamiltonian in the form of Eq. (3) as long as we only want to use it to calculate the wave function to first order. Higher order corrections seem to be model dependent, but have never been calculated. Still, it is probably

not misleading to use Eq. (3) to higher order, as Josephson has done, provided we are interested mainly in phase dependent terms, as explained by Professor Anderson in this volume.

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# Superconductivity with *p*- and *d*-Wave Pairing

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## I. Introduction

We shall survey the properties of a hypothetical superconducting system, in which the pairs would be formed with an angular momentum different from zero. This problem is a generalization of the B.C.S. theory (1), and is conveniently described with a reduced Hamiltonian

$$H \equiv \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}} c_{\mathbf{k}\sigma}^{\dagger} c_{\mathbf{k}\sigma} + \frac{1}{2} \sum_{\mathbf{kk}'\sigma\sigma'} V_{\mathbf{kk}'} c_{-\mathbf{k}\sigma}^{\dagger} c_{\mathbf{k}\sigma}^{\dagger} c_{\mathbf{k}'\sigma'}^{\dagger} c_{-\mathbf{k}'\sigma'}, \quad (1)$$

where

$$V_{\mathbf{kk}'} \equiv \sum_l (2l+1) P_l(\hat{\mathbf{k}} \cdot \hat{\mathbf{k}'}) V_l(k, k'). \quad (2)$$

Here  $c_{\mathbf{k}\sigma}^{\dagger}$  is the fermion creation operator for a plane wave of momentum  $\mathbf{k}$  and spin  $\sigma$ , and the interaction is truncated to particles of total momentum zero. In the B.C.S. theory, only the  $l=0$  term of the expansion (2) of  $V_{\mathbf{kk}'}$  in spherical harmonics is considered; when this term is attractive, although it is a small part of the real interaction, it causes the particles to bind in pairs of total linear momentum, total spin, and angular momentum zero, which condense. The more general case of interaction (2) has been studied in a number of papers which we shall review.

As presented here, this problem looks rather academic, but it has in fact some physical interest. Superconductivity with  $l \neq 0$  may perhaps exist in nature in two different circumstances: metals and liquid He<sup>3</sup>.

### A. METALS

It has been shown in Anderson's lectures that the interaction between electrons arising from the exchange of one phonon has a short range, of the order of magnitude of the lattice spacing. If this range was zero, the Fourier transform of the potential would be a constant, so that Eq. (2) would contain only the term  $l = 0$  considered in the B.C.S. theory. Since the range of the potential is the lattice spacing, its Fourier transform may vary in momentum space over distances of the order of the inverse lattice spacing, that is of the Fermi momentum. Therefore, for  $k \simeq k' \simeq k_F$ , the first few  $l \neq 0$  terms in Eq. (2) may be as large as the  $l = 0$  one. It is thus interesting to study the properties of such a system, in order to be able to recognize it experimentally (if it exists), and to know in which conditions it may be observed.

In fact, the model problem (1) and (2) is an oversimplification of the real one. In particular, the interaction between electrons is retarded, and is furthermore not invariant by rotation (as well as the kinetic energy  $\varepsilon_k$ ). But since the qualitative predictions of the theory are not affected by these facts, we shall simply discuss here the model (1, 2), in particular in the case of an  $l = 1$  attraction.

### B. LIQUID He<sup>3</sup>

Another Fermi system to which the B.C.S. theory may be extended is liquid He<sup>3</sup> (2). Here, the interaction (2) between atoms, for momenta  $k$  and  $k'$  close to  $k_F$ , is repulsive for  $l = 0$  and  $l = 1$ , and attractive for  $l = 2$ . This point is easy to understand: if a potential  $V(r)$  is strongly repulsive for  $r < r_1$  and has a long but weak attractive tail (for  $r_1 < r < r_2$ ), its Fourier transform  $V(q)$  has the shape represented in Fig. 1. Then, since (as functions of the angle  $\widehat{k}, \widehat{k'}$ , and therefore of  $q = |\mathbf{k} - \mathbf{k}'| \simeq 2k_F \sin [\frac{1}{2}\widehat{k}, \widehat{k'}]$ )  $P_0$  is positive,  $P_1$  decreases, and  $P_2$  has a minimum, it is clear from Fig. 1 that  $V_0$  and  $V_1$  are positive and  $V_2$  is negative, provided the density (proportional to  $k_F^3$ ) is large enough, which is the case in liquid He<sup>3</sup>. The more detailed treatments confirm this rough argument. Liquid He<sup>3</sup> at low temperature is well described by the Landau theory. The relevant interaction is that between quasi particles, and it is also repulsive for  $l = 0, 1$ , and attractive for  $l = 2$ .

We shall only consider here the case of an attractive potential in a single partial wave  $l = 1$  (3) or  $l = 2$  (2). In fact, it can be shown that, when several waves are present in Eq. (2), only the most attractive partial

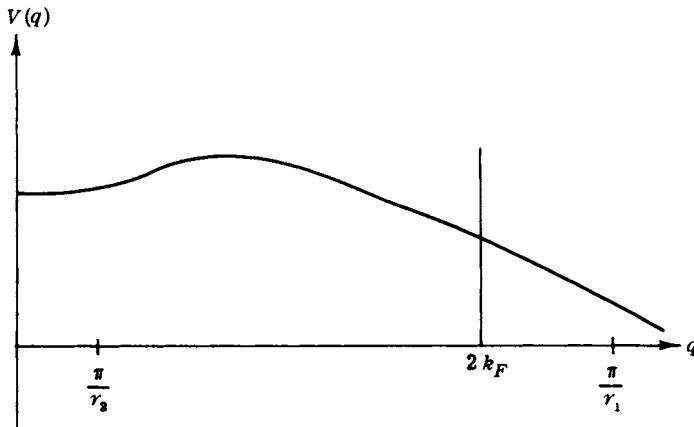


FIG. 1. Variation of the potential  $V(q)$  in momentum space.

wave is relevant, at least for a weak coupling. In particular, all partial waves in the gap equation decouple at  $T = T_c$ , so that the critical temperature depends only on the strength of the most attractive one.

## II. The $p$ -Wave Pairing

### A. THEORY

Equation (2) has the form

$$V_{\mathbf{k}\mathbf{k}'} = -3 \hat{\mathbf{k}} \cdot \hat{\mathbf{k}'} V_1(k, k'), \quad (3)$$

where  $\hat{\mathbf{k}}$  is the unit vector in the direction  $\mathbf{k}$ . Contrarily to the B.C.S. case, the pairing must not be performed between states of opposite spins. Note that the gap matrix

$$\Delta_{\mathbf{k}\sigma\sigma'} \equiv - \sum_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} \langle c_{\mathbf{k}'\sigma} c_{-\mathbf{k}'\sigma'} \rangle \quad (4)$$

plays the role of a bound pair wave function. If  $V_{\mathbf{k}\mathbf{k}'}$  has the form of

Eq. (3), the spatial part of  $\mathcal{J}$  is a combination of spherical harmonics  $l = 1$ , that is of  $k_x, k_y, k_z$ ; its spin part is expected to be a combination of the triplet wave functions. We need therefore a kind of pairing in which all three components of the triplet,  $\uparrow\uparrow$ ,  $\downarrow\downarrow$ , and  $\uparrow\downarrow + \downarrow\uparrow$  are allowed. Pairing spins of the same direction would give only the two first components, and pairing opposite spins would give only the third component of the triplet (and the singlet). It is therefore necessary to introduce a more complicated pairing, which mixes all four operators  $c_{k\uparrow}, c_{k\downarrow}, c_{-k\uparrow}^\dagger$ , and  $c_{-k\downarrow}^\dagger$ .

It is convenient for this purpose to use a matrix notation (4); (also see Kadanoff, this volume). Generalizing the  $2 \times 2$  matrix Green's function which involves both normal and abnormal Green's functions, we define the  $4 \times 4$  matrix Green's function  $\mathcal{G}_k$ , for operators

$$\mathcal{G}_k = \begin{pmatrix} c_{k\uparrow} \\ c_{k\downarrow} \\ c_{-k\uparrow}^\dagger \\ c_{-k\downarrow}^\dagger \end{pmatrix}$$

at time  $t$ , and

$$\mathcal{G}_k^\dagger = (c_{k\uparrow}^\dagger \ c_{k\downarrow}^\dagger \ c_{-k\uparrow} \ c_{-k\downarrow})$$

at time 0.

The equation of motion for  $\mathcal{G}_k$  is obtained by the usual method as

$$(\omega - \mathcal{E}_k) \mathcal{G}_k = 1, \quad (6)$$

where  $\mathcal{E}_k$  is the  $4 \times 4$  matrix

$$\mathcal{E}_k = \left( \begin{array}{cc|cc} \varepsilon_k & 0 & A_{k\sigma\sigma'} & \\ 0 & \varepsilon_k & -\varepsilon_k & 0 \\ \hline (\mathcal{A}_{k\sigma\sigma'})^\dagger & & 0 & -\varepsilon_k \end{array} \right), \quad (7)$$

so that the spectral density is  $\delta(\omega - \mathcal{E}_k)$ .

Through Eq. (4),  $\mathcal{J}$  depends on the anomalous part of the matrix  $\langle \mathcal{G}_k \mathcal{G}_k^\dagger \rangle$ , which is determined self consistently in terms of the spectral density by

$$\langle \mathcal{G}_k \mathcal{G}_k^\dagger \rangle = \int_{-\infty}^{+\infty} d\omega f(\omega) \delta(\omega - \mathcal{E}_k) = f(\mathcal{E}_k) \equiv \frac{1}{2} (1 + \tanh \frac{1}{2} \beta \mathcal{E}_k). \quad (8)$$

It remains now to solve the coupled Eqs. (4, 7, 8).

Let us first consider in this formalism the case when (2) contains only even  $l$ 's. The gap matrix (4) has then the form

$$\mathcal{A}_{\mathbf{k}\sigma\sigma'} = \begin{pmatrix} 0 & \mathbb{1}_{\mathbf{k}} \\ -\mathbb{1}_{\mathbf{k}} & 0 \end{pmatrix}, \quad (9)$$

and it is easy to see that

$$\mathcal{E}_{\mathbf{k}}^2 = \varepsilon_{\mathbf{k}}^2 + |\mathbb{1}_{\mathbf{k}}|^2 = E_{\mathbf{k}}^2 \quad (10)$$

is proportional to the unit matrix. The calculation of  $\text{th } \frac{1}{2} \beta \mathcal{E}_{\mathbf{k}}$  in (8) is thus greatly simplified, since

$$\begin{aligned} \text{th } \frac{1}{2} \beta \mathcal{E}_{\mathbf{k}} &= \mathcal{E} \left( 1 - \frac{1}{3} \mathcal{E}^2 + \frac{2}{15} \mathcal{E}^4 - \dots \right) = \mathcal{E} \left( 1 - \frac{1}{3} E^2 + \frac{2}{15} E^4 - \dots \right) \\ &= \mathcal{E}_{\mathbf{k}} \text{th } \frac{1}{2} \beta E_{\mathbf{k}} / E_{\mathbf{k}}, \end{aligned} \quad (11)$$

and the gap equation

$$\mathcal{A}_{\mathbf{k}} = -\frac{1}{2} \sum_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} \mathbb{1}_{\mathbf{k}'} \text{th } \frac{1}{2} \beta E_{\mathbf{k}'} / E_{\mathbf{k}'} \quad (12)$$

follows.

Returning to the case  $l = 1$ , we make the statement (which will be verified later) that  $\mathcal{E}_{\mathbf{k}}^2$  is still proportional to the unit matrix. Since

$$\mathcal{E}_{\mathbf{k}}^2 = \varepsilon_{\mathbf{k}}^2 + \mathcal{A}_{\mathbf{k}\sigma\sigma'} (\mathcal{A}_{\mathbf{k}\sigma\sigma'})^\dagger \quad (= E_{\mathbf{k}}^2) \quad (13)$$

this assumption amounts to suppose that  $\mathcal{A}$  is proportional to a unitary matrix. Then (11) holds, and we get as a consequence of (7) and (8)

$$\langle c_{\mathbf{k}\sigma} c_{-\mathbf{k}\sigma'} \rangle = \frac{1}{2} \mathcal{A}_{\mathbf{k}\sigma\sigma'} \text{th } \frac{1}{2} \beta E_{\mathbf{k}} / E_{\mathbf{k}}, \quad (14)$$

which together with (4) leads to the gap equation

$$\mathcal{A}_{\mathbf{k}\sigma\sigma'} = -\frac{1}{2} \sum_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} \mathcal{A}_{\mathbf{k}'\sigma\sigma'} \text{th } \frac{1}{2} \beta E_{\mathbf{k}'} / E_{\mathbf{k}'} . \quad (15)$$

It is easy to check that Eq. (15) [with  $V_{\mathbf{k}\mathbf{k}'}$  given by (3)] admits as a solution

$$\mathcal{A}_{\mathbf{k}\sigma\sigma'} = \delta_k \begin{pmatrix} -\hat{k}_x + i\hat{k}_y & \hat{k}_z \\ \hat{k}_z & \hat{k}_x + i\hat{k}_y \end{pmatrix} \quad (16)$$

in which

$$\delta_k = \frac{1}{2} \sum_{\mathbf{k}'} V_1(k, k') \delta_{k'} \text{th } \frac{1}{2} \beta E_{k'} / E_{k'} \quad (17)$$

is the same as the gap equation (12) which would correspond to an *s*-wave potential  $V_1(k, k')$ . Finally, we verify that Eq. (12) is satisfied, since (16) implies  $\Delta\Delta^\dagger = |\delta_k|^2$ . Moreover, as is well known, the present Green's functions treatment is equivalent to the variational approach of B.C.S.-Bogoliubov (*I*), and it may be shown that the solution (16, 17) leads to the lowest free energy, so that the statement is fully justified.

### B. COMPARISON WITH THE B.C.S. CASE

The quasi-particle energy

$$E_k = (\varepsilon_k^2 + |\delta_k|^2)^{1/2} \quad (18)$$

has the same form as in the B.C.S. theory, and the resulting properties (gap, specific heat, tunneling characteristics) will therefore be the same. It is also easy to show that the state with *p*-wave pairs would present no Meissner effect.

The isotropy of this state and of the energy (18) can be understood by rewriting (16) as

$$\Delta_{\mathbf{k}\sigma\sigma'} \propto \sum_m \left\langle \frac{1}{2} \frac{1}{2} \sigma\sigma' \mid 1m \right\rangle Y_{1m}(\mathbf{k}) \langle 1m 1m' \mid 00 \rangle \quad (19)$$

which shows that  $\Delta_{\mathbf{k}\sigma\sigma'}$  behaves like the wave function of a pair with total spin 1, orbital angular momentum 1, coupled together to a total angular momentum zero. (In the B.C.S. case, both total spin and orbital angular momentum vanish.)

Although the pairs are isotropic, they have a spin 1. As a first consequence, there exists a set of low lying collective states, constructed by rotating the spins with respect to the angular variables. These states, which have no equivalent in the B.C.S. theory, would, however, be difficult to detect.

A more remarkable difference with the B.C.S. case is the spin susceptibility (Fig. 2). In the B.C.S. case, it is necessary to provide a finite energy in order to flip a spin, since a pair must be broken, so that the spin susceptibility vanishes at  $T = 0$ . Here 1/3 of the pairs are in a state  $m_s = 0$  and behave like B.C.S. pairs, but the remaining 2/3 are coupled to a spin component  $m_s = \pm 1$ ; applying a weak magnetic field changes the population of these pair states, without breaking the pairs, so that 2/3 of the particles behave as if they were free, and the spin

susceptibility at  $T = 0$  is predicted to be  $2/3$  of the normal spin susceptibility. It is curious to note the agreement between the predictions of this  $l = 1$  theory with experiments performed in Sn and Hg (Fig. 2).

It is thus tempting to conclude that in these materials  $V_{kk'}$  is more attractive for the  $p$ -wave than for the  $s$ -wave, since other experiments

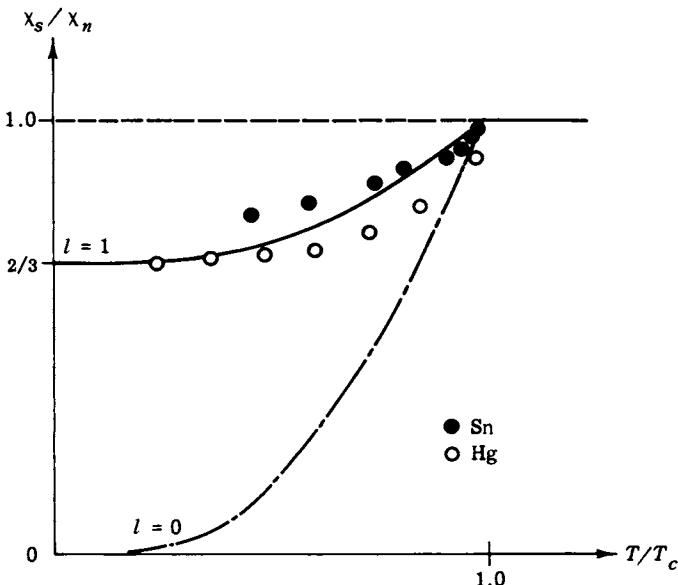


FIG. 2. Spin susceptibility  $\chi$  of a superconductor with  $l = 0$  and  $l = 1$ .

do not allow the distinction between  $s$ -and  $p$ -wave pairing. However, the experimental situation is not very clear; it is now believed that the anomalous Knight shift experiments are not a measurement of the spin susceptibility of conduction electrons only, and the agreement is probably a coincidence.

On the other hand, another difference with the B.C.S. case comes from the fact that the radial pair wave function has  $l = 1$  instead of  $l = 0$ , so that the pairs are more loosely bound. As a consequence, impurities will have an important effect. The dirty superconductor theorem (see Anderson's lectures) does not apply here, since it is based on two hypotheses: the scattering is invariant by time reversal (which is true for nonmagnetic impurities), and the interaction is local (which is

true in the B.C.S. case, but not here). Each nonmagnetic impurity, as well as dislocation, surface effects, etc. ... will have a strong effect, comparable with a magnetic impurity in the B.C.S. case. Since the density of nonmagnetic impurities is very large, they will affect considerably the critical temperature, contrary to the *s*-wave case.

The observation of superconductivity with *p*-wave pairing, which is expected to occur if the particles attract more in the *p*-wave than in the *s*-wave, is therefore probably very difficult, since very pure and perfect samples are needed. The simplest way of distinguishing such a state from an *s*-wave state is to detect strong impurity effects.

### III. The *d*-Wave Pairing

In the case of an  $l = 2$  attractive potential

$$V_{\mathbf{k}\mathbf{k}'} = -5 P_2(\hat{\mathbf{k}} \cdot \hat{\mathbf{k}'}) V_2(k, k') , \quad (20)$$

the solutions of the gap equations (10, 12) have an angular dependance (2) of the form

$$\mathcal{A}_{\mathbf{k}} = \sum_m c_m Y_{2m}(\hat{\mathbf{k}}) . \quad (21)$$

Anderson and Morel found that the solution of lowest energy is obtained for the combination

$$c_1 = c_{-1} = 0 \quad c_2 = -c_{-2} = c_0 / \sqrt{2} ,$$

that is for

$$\mathcal{A}_{\mathbf{k}} \propto k_x^2 + j k_y^2 + j^2 k_z^2 \quad (j^3 = 1) . \quad (22)$$

Contrary to the case  $l = 1$ , most predicted properties differ from those of  $l = 0$ . First, the gap vanishes, since (22) is equal to zero in the directions  $k_x = \pm k_y = \pm k_z$ . It results that the specific heat will behave like  $T^3$  at low temperature, instead of  $e^{-1/T}$ . The state is anisotropic, somewhat as in the case of a ferromagnet or a solid, and the energy  $E_{\mathbf{k}}$  of the elementary excitations depends on the direction  $\mathbf{k}$ ; the symmetry of the state is that of a cube, as seen in (22). The detection of such a superfluid phase of  $\text{He}_3$  is therefore expected to be easy.

Two problems have been raised by this theory. The first one is purely

theoretical, and concerns the treatment of the model Hamiltonian (1, 2): Gorkov and Galitskii (5), using another method than above, have found a ground state with different properties (in particular isotropy). It is therefore interesting to compare both methods and find which one is correct. The second problem is to explain why the predicted phase has not yet been observed experimentally.

### A. THE METHOD OF GORKOV AND GALITSKII

In terms of normal and abnormal Green's functions  $G_{\mathbf{k}}$  and  $F_{\mathbf{k}}$ , Eqs. (6, 9) are rewritten as

$$\begin{aligned} (\omega - \varepsilon_k) G_{\mathbf{k}} - A_{\mathbf{k}} F_{\mathbf{k}}^+ &= I \\ (\omega + \varepsilon_k) F_{\mathbf{k}}^+ - A_{\mathbf{k}}^* G_{\mathbf{k}} &= 0. \end{aligned} \quad (23)$$

These equations may also be obtained without introducing anomalous Green's functions  $F$ . Consider the hierarchy of equations satisfied by the higher order Green's functions  $G$ ,  $G^{(2)}$ ,  $G^{(3)}$ , .... Rewriting them in terms of the connected parts  $G$ ,  $C^{(2)}$ ,  $C^{(3)}$ , ... defined as usual, we neglect  $C^{(3)}$  in the equation satisfied by  $C^{(2)}$ , and assume that the correlation function  $C^{(2)}$  for states of opposite momenta and spins is factorizable into  $F_{\mathbf{k}}^+ F_{\mathbf{k}}$ . Then, Eq. (23) are recovered as the two first equations of the hierarchy.

This way of presenting the B.C.S. theory has been generalized by G.G. Assuming a nonseparable  $C^{(2)}$ , of the form  $\sum_m F_{\mathbf{k}m}^+ F_{\mathbf{k}'m}$ , and still neglecting  $C^{(3)}$ , Eq. (23) are replaced by

$$(\omega - \varepsilon_k) G_{\mathbf{k}} - \sum_m A_{\mathbf{km}} F_{\mathbf{km}}^+ = I \quad (24a)$$

$$\sum_m F_{\mathbf{k}'m} \{(\omega + \varepsilon_k) F_{\mathbf{km}}^+ - A_{\mathbf{km}}^* G_{\mathbf{k}}\} = 0, \quad (24b)$$

where

$$A_{\mathbf{km}} = - \sum_{\mathbf{k}'} V_{\mathbf{kk}'} \int_{-\infty}^{+\infty} d\omega \varrho_{\mathbf{k}'m} f(\omega) \quad (25)$$

[ $\varrho_{\mathbf{km}}$  is the spectral density associated with  $F_{\mathbf{km}}(\omega)$ ]. The quasi-particle energy [introduced by solving Eq. (24)] is now

$$E_{\mathbf{k}}^2 = \varepsilon_k^2 + \sum_m |A_{\mathbf{km}}|^2, \quad (26)$$

and  $\Delta_{\mathbf{k}m}$  is a solution of

$$\Delta_{\mathbf{k}m} = -\frac{1}{2} \sum_{\mathbf{k}'} V_{\mathbf{kk}'} \Delta_{\mathbf{k}'m} \operatorname{th} \frac{1}{2} \beta E_{\mathbf{k}'} / E_{\mathbf{k}'} . \quad (27)$$

This gap equations (26, 27) differs from the usual one (10, 12), if  $m$  takes several values. In particular, for  $l = 2$  (Eq. 20), G.G. find

$$\Delta_{\mathbf{k}m} = Y_{lm}(k) (4\pi/5)^{\frac{1}{2}} \Delta_k \quad (28)$$

$$E_k^2 = \varepsilon_k^2 + |\Delta_k|^2 \quad (29)$$

$$\Delta_k = \frac{1}{2} \sum_{\mathbf{k}'} V_2(k, k') \Delta_{\mathbf{k}'} \operatorname{th} \frac{1}{2} \beta E_{\mathbf{k}'} / E_{\mathbf{k}'} . \quad (30)$$

Contrary to the solution of A.M. [Eqs. (10, 22)] this solution is isotropic. The gap is  $\Delta_k$  and does not vanish. Equation (30) has the same form as in the  $l = 0$  case, which gives a free energy lower than in the theory of A.M. (Fig. 3). The critical temperatures are the same in both theories.

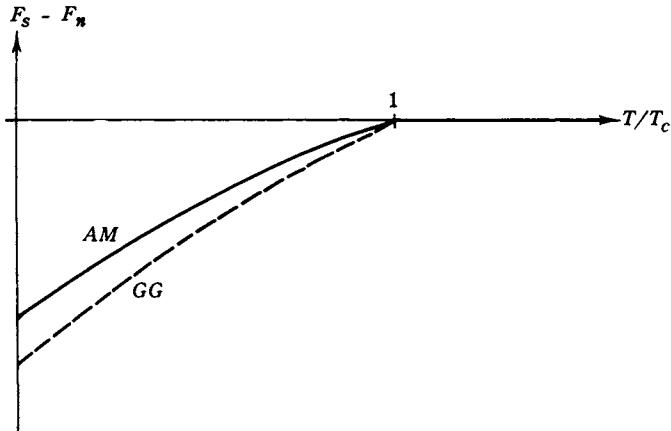


FIG. 3. Free energy of a superconducting system with  $l = 2$ , as predicted in the theories of Anderson and Morel, and Gorkov and Galitskii.

If the treatment of G.G. was variational, we would conclude from Fig. 3 that it is a better approximation than the A.M. solution (which is variational, as is well known). This, however, is not the case (6).

In fact, one can prove that in the limit of an infinite volume, the ground state energy per unit volume given by the A.M. theory is asymptotically exact for the model Hamiltonian (1) considered here, whereas the energy given by the G.G. theory is lower by a finite amount from the exact ground state energy.

The method of G.G., although it appears like a natural extension of the B.C.S. theory, is therefore not correct. It is interesting to try to understand why this is so, and why  $C^{(2)}$  cannot be taken as separable when  $C^{(3)}$  is neglected. Let us consider the third equation in the hierarchy, which must be satisfied by  $C^{(3)}$ . We do not write it explicitly, but represent each term by a diagram (Fig. 4), dropping the terms in  $1/\Omega$ .

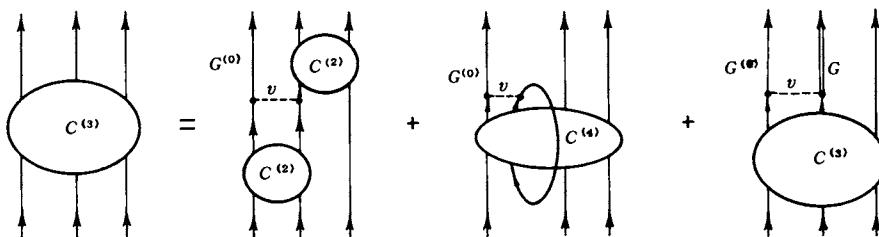


FIG. 4. Third equation of the hierarchy.

From this equation, it is clear that  $C^{(3)}$  and  $C^{(4)}$  cannot both be small if  $C^{(2)}$  is large. In particular, the B.C.S. theory is asymptotically exact for  $\Omega \rightarrow \infty$  [as seen by considering the hierarchy of coupled equations, written now in terms of both normal and anomalous Green's functions and corresponding connected parts (7)]. In this case,  $C^{(3)} = 0$ , which implies that  $C^{(4)}$  is such that the two first terms of Fig. 4 compensate exactly. In this formalism without anomalous Green's functions, such a cancellation appears as a coincidence [since  $C^{(3)} = 0$ , but  $C^{(4)} \neq 0$  in the B.C.S. case]; it becomes impossible if  $C^{(2)}$  is not separable, so that  $C^{(3)}$  cannot be neglected in the second equation (24b) of the hierarchy [giving  $C^{(2)}$ ].

It remains, however, an open question whether the treatment of G.G. would be correct in the case of a Hamiltonian more general than (1).

### B. ADEQUACY OF THE MODEL

The theories (2, 5) based on the reduced Hamiltonian (1) predict a critical temperature between 0.1 and 0.05°K. However, liquid He<sup>3</sup> has been studied down the 0.008°K, and no transition has been found. The model used is therefore too crude to describe liquid He<sup>3</sup>, and several attempts, none completely successful, have been made to explain the absence of transition.

The predicted temperature is reduced, but not enough, if lifetime effects are taken into account (8). Due to collisions, quasi particles are not stable, and the pairing may take place only during their lifetime. This effect is taken into account by introducing a peaked spectral density instead of the  $\delta$ -function density used above, with a width taken from scattering experiments.

On the other hand, nonmagnetic impurities as well as elastic scattering have a strong effect, as in the case  $l = 1$ , and experiments have always been performed in impure liquid He<sup>3</sup>. It is also possible that three-particle correlations, which are much more important for liquid He<sup>3</sup> than for an electron gas in a metal, tend to destroy the formation of pairs. Because no precise calculation has been done, theory and experiment do not yet agree.

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# Electrons in Disordered Systems

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## I. Introduction

The subject of this paper is the behavior of electrons in systems for which the potential is not completely determined as a function of position, but is instead given by some probability distribution. The electrons will be assumed to be independent, so that the problem reduces to that of one electron. The available states are then filled with due regard to the Pauli principle. This formalism, developed by S. F. Edwards, applies equally well to independent quasi particles moving in an appropriate potential.

Consider a set of identical ions fixed at positions  $\mathbf{R}_i$ ,  $i = 1, 2, \dots, N$ . If the potential around each ion is  $v(\mathbf{r})$ , the Schrodinger equation is

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + \sum_a v(\mathbf{r} - \mathbf{R}_a) - E_n \right] \psi_n(\mathbf{r}) = 0$$

and the propagator for the electron in this potential is

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + \sum_a v(\mathbf{r} - \mathbf{R}_a) - E - i\epsilon \right] G(\mathbf{r}, \mathbf{r}'; E) = -\delta(\mathbf{r} - \mathbf{r}')$$

and is given in terms of  $\psi_n$  by

$$G(\mathbf{r}, \mathbf{r}'; E) = \sum_n \frac{\psi_n(\mathbf{r}) \psi_n^*(\mathbf{r}')}{E - E_n + i\epsilon}. \quad (1)$$

Now consider a system of such sets in which the particular set  $\mathbf{R}_1, \dots, \mathbf{R}_N$  occurs with a probability distribution  $P(\mathbf{R}_1, \dots, \mathbf{R}_N)$ . The average of

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any function over this system will be denoted by Dirac brackets which thus correspond to the integration of the function with  $P$  over all  $\mathbf{R}_1, \dots, \mathbf{R}_N$  space. Such a system may be formed by subdividing the given substance into a large number of smaller pieces or by taking the whole of the substance and considering its instantaneous distribution at different times. (There is no time dependence in the theory, which is therefore entirely within the adiabatic approximation.)

Take the Fourier transformation of (1), average it over the system, and take its imaginary part:

$$\langle \text{Im } G(\mathbf{k}, \mathbf{k}; E) \rangle = -\pi \left\langle \sum_n \psi_n(\mathbf{k}) \psi_n^*(\mathbf{k}) \delta(E - E_n) \right\rangle$$

(the two transformed variables have been put equal). The right-hand side is then the probability that in this system a state with energy  $E = E_n$  has "momentum"  $\mathbf{k}$ . In other words the density of states with a given energy and momentum is a probability distribution

$$\varrho(\mathbf{k}, E) = -\text{Im } \pi^{-1} \langle G(\mathbf{k}, \mathbf{k}; E) \rangle$$

and the density of levels is now

$$n(E) = \int \varrho(\mathbf{k}, E) d\mathbf{k}$$

In an ordered system the brackets do not arise and if the spectrum is continuous one has  $\varrho(\mathbf{k}, E) \propto \delta[E - E(\mathbf{k})]$ , i.e.,  $E$  and  $\mathbf{k}$  are directly related.

Our program will be to work out the propagator  $G(\mathbf{k}, \mathbf{k}; E)$  and from it to evaluate the density of states. Transport properties such as conductivity, in general require averages over pairs of propagators and so are much harder to work out.

The technique to be used is that of formally expanding the propagator around the unperturbed propagator  $G_0$  which satisfies

$$\left( -\frac{\hbar^2}{2m} \nabla^2 - E - i\varepsilon \right) G_0(\mathbf{r} - \mathbf{r}'; E) = -\delta(\mathbf{r} - \mathbf{r}').$$

In Fourier transform  $G_0(\mathbf{k}; E) = (E - k^2 + i\varepsilon)^{-1}$ . The expansion may then be averaged term by term and the series re-summed in an appropriate manner.

Thus

$$\langle G \rangle = G_0 + G_0 \langle \sum_a v_a \rangle G_0 + G_0 \langle \sum_a v_a G_0 \sum_\beta v_\beta \rangle G_0 + \dots . \quad (2)$$

Consider first the case of weak potentials.

## II. Weak Potentials

If the potential is weak then it is convenient to choose the zero of energy to be such that  $\langle \sum_a v_a \rangle = 0$  (in the case of a homogeneous system), after which all terms involving odd powers of the potential will in general be small compared to the term following which has one extra power of  $v$ . If one now writes

$$\langle \sum_a v_a G_0 \sum_\beta v_\beta \rangle = \Sigma_2$$

and

$$\langle \sum_a v_a G_0 \sum_\beta v_\beta G_0 \sum_\gamma v_\gamma G_0 \sum_\delta v_\delta \rangle = \Sigma_2 G_0 \Sigma_2 + \Sigma_4$$

and so on, then a formally exact summation of Eq. (2) is given by

$$\langle G \rangle = (G_0^{-1} - \Sigma_2 - \Sigma_4 - \dots)^{-1}.$$

If  $\Sigma_4$  is small compared with  $\Sigma_2$  and is, in particular, well behaved near the zeros of  $G_0^{-1} - \Sigma_2$ , then this formal summation may be a good approximation to the correct answer. This approximation depends mainly on the degree of order in the system; it is very good for a random system or for a perfect lattice. The remaining step is to work out  $\Sigma_2$  and the two extreme cases may be used to illustrate this process.

### A. COMPLETE DISORDER

In Fourier transform

$$\begin{aligned} \Sigma_2 &= \langle \sum_{\alpha\beta} v(\mathbf{x} - \mathbf{R}_\alpha) G_0(\mathbf{x} - \mathbf{y}) v(\mathbf{y} - \mathbf{R}_\beta) \rangle \\ &= \langle \sum_{\alpha\beta} \left( \frac{1}{2\pi} \right)^6 v(\mathbf{k}) v(\mathbf{j}) \exp(i\mathbf{k} \cdot \mathbf{R}_\alpha + i\mathbf{j} \cdot \mathbf{R}_\beta) \rangle \\ &\quad \int \exp(-i\mathbf{k} \cdot \mathbf{x}) \exp(-i\mathbf{j} \cdot \mathbf{y}) G_0(\mathbf{x} - \mathbf{y}) d\mathbf{x} d\mathbf{y} \end{aligned}$$

so that the averaging is concentrated into

$$\left\langle \sum_{\alpha\beta} \exp(i\mathbf{k}\cdot\mathbf{R}_\alpha + i\mathbf{j}\cdot\mathbf{R}_\beta) \right\rangle \delta(\mathbf{k} + \mathbf{j}) .$$

If the  $\mathbf{R}$ 's are completely random only the  $\alpha = \beta$  terms in the sum survive and then

$$\delta(\mathbf{k} + \mathbf{j}) \left\langle \sum_{\alpha\beta} \exp(i\mathbf{k}\cdot(\mathbf{R}_\alpha - \mathbf{R}_\beta)) \right\rangle = N$$

so that

$$\Sigma_2 = \frac{N}{(2\pi)^3 V} \int |v(\mathbf{j})|^2 G_0(\mathbf{j}) d\mathbf{j} .$$

At the same time  $\Sigma_4$  depends on

$$\left\langle \sum_{\alpha,\beta,\gamma,\delta} \exp(i\mathbf{l}\cdot\mathbf{R}_\alpha + i\mathbf{m}\cdot\mathbf{R}_\beta + i\mathbf{n}\cdot\mathbf{R}_\gamma + i\mathbf{p}\cdot\mathbf{R}_\delta) \right\rangle$$

of which the dominant terms occur when  $\alpha = \beta$ ,  $\gamma = \delta$  (the  $\Sigma_2 G_0 \Sigma_2$  part) and when  $\alpha = \gamma$ ,  $\beta = \delta$  or  $\alpha = \delta$ ,  $\beta = \gamma$ . These last two choices lead to terms of the form

$$\frac{N^2}{V^2} \int |v(\mathbf{j})|^2 |v(\mathbf{l})|^2 G_0(\mathbf{k} - \mathbf{j}) G_0(\mathbf{k} - \mathbf{l} - \mathbf{j}) G_0(\mathbf{k} - \mathbf{j}) d\mathbf{j} d\mathbf{l}$$

which have no poles. In this case one may show that

$$\frac{\Sigma_4}{\Sigma_2} = 0 \left( \frac{\text{Potential scattering length}}{\text{Electron wavelength}} \right).$$

## B. PERFECT ORDER

In a perfect lattice with one atom per unit cell

$$\left\langle \sum_{\alpha,\beta} \exp[i\mathbf{k}\cdot(\mathbf{R}_\alpha - \mathbf{R}_\beta)] \right\rangle = \frac{N^2}{V} \frac{1}{(2\pi)^3} \sum_{\mathbf{K}} \delta(\mathbf{k} - \mathbf{K})$$

where the  $\mathbf{K}$  are the reciprocal lattice vectors. Therefore

$$\Sigma_2 = \frac{N^2}{V^2} \sum_{\mathbf{K}} \frac{|v(\mathbf{K})|^2}{E - \frac{\hbar^2}{2m} (\mathbf{k} - \mathbf{K})^2} .$$

The zeros of  $G_0^{-1} - \Sigma_2$  then lie along the lines in  $E, k$  space illustrated by Fig. 1 in the case of one dimension.

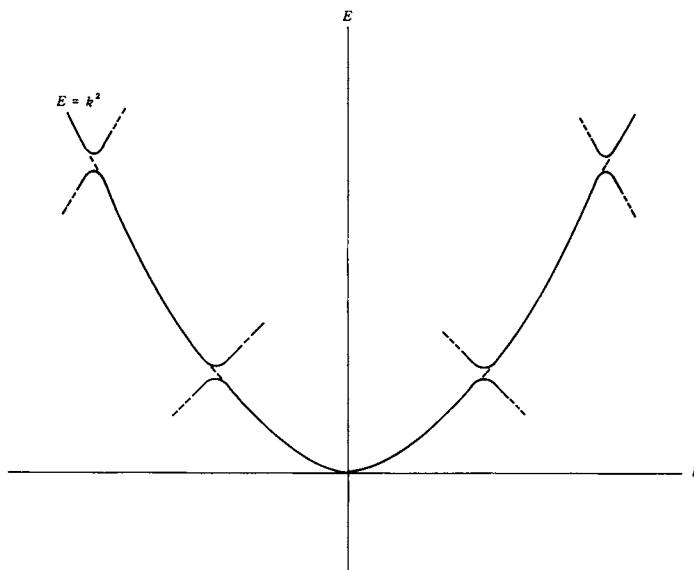


FIG. 1. One-dimensional perfect lattice.

The gaps are correct along the  $E = k^2$  curve, but away from  $E = k^2$  the curves are incorrect. The  $\Sigma_4$  and higher terms would serve to reintroduce the periodicity in reciprocal space. It is important to note, however, that even in the case of the perfect lattice the  $E, k$  diagrams such as that given in Fig. 1 are not extended Brillouin zone pictures.

### III. Polycrystalline Materials

The “geometric approximation” which makes the fourth order term  $\approx \Sigma_2 G_0 \Sigma_2$  breaks down completely in the case of a material consisting of randomly orientated perfect crystals. In this case

$$\langle \sum_{\alpha\beta} \exp[i\mathbf{k} \cdot (\mathbf{R}_\alpha - \mathbf{R}_\beta)] \rangle = \frac{N^2}{V} \frac{1}{(2\pi)^3} \frac{1}{4\pi} \int d\Omega_{\mathbf{k}} \sum_{\mathbf{K}} \delta(\mathbf{k} - \mathbf{K})$$

and the term which was  $\Sigma_2 G_0 \Sigma_2$  is now

$$\left[ \frac{N^2}{V} \frac{1}{(2\pi)^3} \right]^2 \frac{1}{4\pi} \int d\Omega_{\mathbf{k}} \sum_{\mathbf{K}\mathbf{K}'} \delta(\mathbf{k} - \mathbf{K}) \delta(\mathbf{j} - \mathbf{K}')$$

which bears no resemblance to the  $(\Sigma_2)^2$  term.

In this case and that of a liquid with true order, one must leave the angular integration (or averaging) until after the summation has been done. Thus one takes the local structure to have a certain fixed direction (the same for all parts of the liquid) and sums the series. The fixed direction is then averaged over.

There is another important point which needs to be made about the approximation. It is easy to prove that in one dimension a system of  $\delta$ -functions which are such that the nearest neighbor distances are randomly distributed between  $a + b$  and  $a - b$  can possess gaps in their energy spectrum. The theory discussed here is not correct in those gaps — it implies a small (but finite) distribution of states in the gap.

#### IV. Strong Potentials

If the lattice potentials  $v(\mathbf{r})$  are strong, and especially if they are strong enough for there to be bound states of the electrons within them, then it is useful to consider the  $t$ -function

$$t = v + v G_0 v + v G_0 v G_0 v + \dots$$

which sums the repeated scatterings off the potential. This function contains as much information as the electron propagator in the presence of the single potential;  $t$ , when considered as a function of energy, has poles at the bound state energies of  $v$ .

In place of  $G$  for the system, one may use  $T$  which is defined in an analogous manner to  $t$ .  $G$  and  $T$  are related by

$$G(\mathbf{r}, \mathbf{r}') = G_0(\mathbf{r}, \mathbf{r}') + \int G_0(\mathbf{r}, \mathbf{r}'') T(\mathbf{r}'', \mathbf{r'''}) G_0(\mathbf{r'''}, \mathbf{r}') d\mathbf{r}'' d\mathbf{r'''}$$

$T$  possesses more of the crystal symmetries than  $G$ . Then

$$\langle G(\mathbf{k}) \rangle = G_0(\mathbf{k}) + G_0^2(\mathbf{k}) \langle T(\mathbf{k}) \rangle .$$

The origin of energy used to define  $G_0(\mathbf{k})$  is of no physical significance in the infinite system and corresponding to this the effect of the first term on the right-hand side of the equation cancels with the effect of  $G_0^2(\mathbf{k})$  in the second. Thus

$$\text{Im } \langle G(\mathbf{k}) \rangle = (E - \mathbf{k}^2)^{-2} \text{ Im } \langle T(\mathbf{k}) \rangle.$$

The expansion of  $T$  in terms of the  $v_a$  and  $t_a$  is

$$\begin{aligned} T &= \sum_a v_a + \sum_a v_a G_0 \sum_\beta v_\beta + \dots \\ &= \sum_a t_a + \sum_{\alpha \neq \beta} t_\alpha G_0 t_\beta + \sum_{\substack{\alpha \neq \beta \\ \beta \neq \gamma}} t_\alpha G_0 t_\beta G_0 t_\gamma \dots. \end{aligned} \quad (3)$$

No two consecutive  $t$ 's may have the same index. This last fact makes some of the integrals simpler since  $G_0(\mathbf{x})$  is singular at the origin in (three-dimensional) coordinate space and if the potentials do not overlap the second series requires no integrations over the singular point.

## V. Krönig-Penney Model

For a perfect lattice (with one atom per unit cell) the series (3) is exactly geometric. The series can now be summed in a simple manner for the potential  $v(r) = -\lambda \delta(r)$  in one dimension, with lattice spacing  $a$ . This gives, if  $\sigma = N/V$  and  $K = 2\pi/a$

$$\begin{aligned} T(\mathbf{k}) &= \frac{-\sigma\lambda}{1 - (\lambda/2\sqrt{E}) [(\sin\sqrt{E}a)/(\cos\sqrt{E}a - \cos ka)]} \\ &= \frac{-\lambda/a}{1 + (\lambda/a) \sum_{-\infty}^{\infty} 1/[E - (k + nK)^2]}. \end{aligned}$$

The imaginary part is nonzero only when the denominator is zero, i.e.,

$$\cos ka = \cos \sqrt{E}a - \frac{\lambda}{2\sqrt{E}} \sin \sqrt{E}a.$$

This is exactly the usual expression for the Krönig-Penney model.

## VI. Tight-Binding Case

When  $E < 0$  the unperturbed propagator decays exponentially with increasing distance. This leads to an entirely different situation to the case when  $E > 0$ . This distinction does not always have a real physical foundation especially in the perfect lattice case. The decay of the propagator for  $E < 0$  means that the sums in Eq. (3) are weighted toward those terms involving nearest neighbors. This corresponds exactly to tight-binding theory where the exponential decay is provided by the wave functions. One is therefore able to make a consistent approximation by retaining only a certain number of nearest neighbor terms in the sums. In particular it is easy to obtain from the series the normal tight-binding approximation.

Applying the technique to a disordered system one is able to discuss the possibility of gaps in the energy spectrum. The series (3) may be

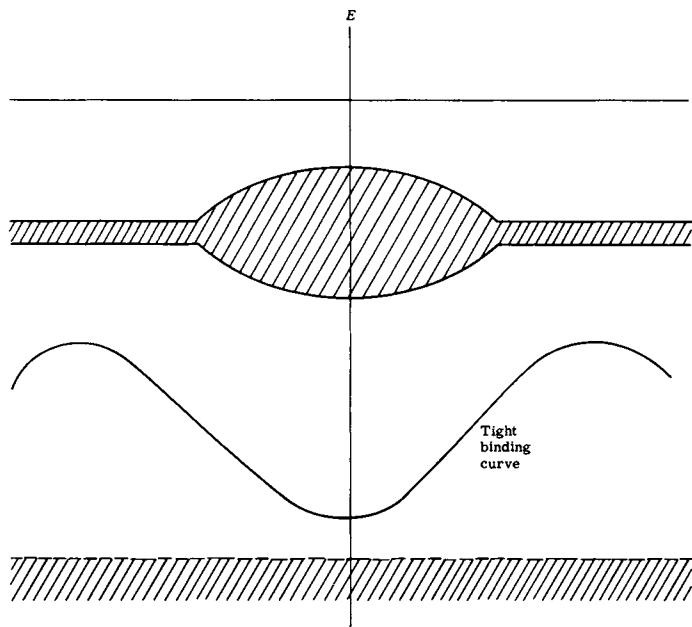


FIG. 2. Regions in which the density of states is zero.

approximately summed to give (formally)

$$T = \sum_a t_a \left( 1 - \frac{\sum_{\alpha \neq \beta} t_\alpha G_0 t_\beta}{\sum_a t_a} \right)^{-1}.$$

The expression in the denominator will be given by a probability distribution in the case of a disordered system, but will be bounded, both above and below provided that the ions do not approach closer than a certain distance. This bounded property leads to the possibility of energy gaps existing in the disordered case. Thus, in one dimension, for a single level, the gap must stay open provided that the minimum distance of approach is greater than a certain value.

The shaded region in Fig. 2 shows where the density of states is identically zero. The result holds also for a single *s*-level in three dimensions and for the region between two *s*-levels in three dimensions.

## VII. Three-Dimensional Problem

Beginning with the series (3), considerable progress can be made by assuming that the potential around each ion is spherically symmetric, and that the region between these spheres is at a constant potential. This means that the coordinates in the *t*-functions on each side of any given  $G_0$  do not overlap. Expanding each *t* in terms of a real angular momentum set  $Y_L(\Omega)$ , enables the integrations to be carried out. This is because the  $G_0$  are free-space propagators in the region of constant potential. Thus if one defines

$$G_{LL'} = \sum_{L''} \sum_{\mathbf{R} \neq 0} Y_{L''}(\mathbf{R}) \exp(-i\mathbf{k} \cdot \mathbf{R}) A_{L''}(R)$$

where  $\mathbf{R}$  are the interatomic distances and  $A(R)$  is a product of radial functions with Clebsch-Gordon coefficients, the geometric approximation gives

$$T(\mathbf{k}) = (4\pi^2) \sum_{LL'} Y_L(\mathbf{k}) Y_{L'}(\mathbf{k}) \{ t_i \delta_{LL'} + [tG(1-tG)^{-1} t]_{LL'} \}.$$

Here the *t*'s are certain transforms of the *t*-function. In this result the dependence on the positions of the ions is entirely within  $G$ , while the

dependence on the shape of the potential is entirely within  $t$ . Thus the two effects have been separated. These remarks do not depend on the nearest neighbor approximation and are equally valid for  $E > 0$  or  $E < 0$ .

Finally one has, if

$$F_{LL'} = G_{LL'} - i\sqrt{E} \delta_{LL'} = F_R + iF_I$$

that

$$\text{Im } T(\mathbf{k}) = (4\pi)^2 \sum_{LL'} Y_L(\mathbf{k}) Y_{L'}(\mathbf{k}) \frac{S_l(k)}{S_l(\sqrt{E})} [M]^{-1} \frac{S_{l'}(k)}{S_{l'}(\sqrt{E})}$$

where

$$M = \left( \frac{\sqrt{E}}{S} + F_R \right) F_I^{-1} \left( \frac{\sqrt{E}}{S} + F_R \right) + F_I.$$

Here  $S_l$  is a function related to  $t_l(x, y)$  and is such that  $S_l(\sqrt{E}) = \tan \eta_l$ . This expression enables the density of states to be calculated for a disordered system. It is not immediately useful in the case of a liquid since  $F$  involves correlation functions of high order which are not known.

In the case of long range order  $F_I$  is a set of  $\delta$ -functions and then  $M$  must be evaluated with particular care. The result is

$$M^{-1} = \pi \text{ cofactor } \left( \frac{\sqrt{E}}{S} + F_R \right) \delta \left( \det \left[ \frac{\sqrt{E}}{S} + F_R \right] \right).$$

In the case of a perfect lattice this result is exact, the density of states being nonzero only when  $\det [(\sqrt{E}/S) + F_R] = 0$ . This equation for the band structure is identical to that of Kohn and Rostoker (5).

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# Oscillations of a Quantum Electron Gas in a Uniform Magnetic Field

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## I. Introduction

Recent experimental efforts to extract information on the electronic structure of metals have involved such techniques as the measurement of electron cyclotron resonance, or of ultrasonic attenuation in the presence of a magnetic field. As an aid in the theoretical understanding of the behavior of metallic electrons in a magnetic field, we would like to describe some aspects of the much simpler problem of an electron gas in a uniform magnetic field. Although the classical version of this problem has been extensively treated (1, 2, 3, 4), a quantummechanical analysis is necessary if one wishes to apply the results to metallic electrons. The case of ultrasonic attenuation of an electron gas in a uniform magnetic field has been examined in a semiclassical approximation by M. H. Cohen *et al.* (5) and later in the quantummechanical random-phase approximation by Quinn and Rodriguez (6).

From a different point of view, RPA derivations of the spectrum of density oscillations have been given by P. S. Zyryanov (7) and M. Stephen (8). The resulting dispersion relation turns out to have a rather complicated structure, and a considerable amount of additional analysis is required to arrive at a clear picture of what the resonances predicted by the RPA are like. We would like to describe the results of such an analysis in the limit of long wavelengths, giving the location of the resonant frequency, a discussion of their damping, and a semiclassical

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picture of the collective motions involved. We shall only state results, referring the reader to reference (9) for the mathematical details.

## II. RPA Calculation of the Resonances

We can find the resonant frequencies by calculating the response of an electron gas in a uniform magnetic field, initially in thermal equilibrium, to a weak external potential,  $U(\mathbf{r}, t)$ . In the random phase approximation, coulomb interactions between electrons are replaced by a self-consistent single particle potential,

$$V(\mathbf{r}, t) = \int d\mathbf{r}' \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} [\varrho(\mathbf{r}', t) - \varrho^0],$$

where  $\varrho(\mathbf{r}, t)$  is the density of particles, and  $\varrho^0 = N/V$  represents a uniform background of positive charge. The single-particle density matrix  $\varphi$  therefore obeys the equation of motion:

$$i \dot{\varphi} = [H_0 + V + U, \varphi], \quad (1)$$

where  $H_0$  is the Hamiltonian for a single electron in a magnetic field. We look for a solution to Eq. (1) of the form

$$\varphi = \varphi^0 + \varphi^1,$$

where  $\varphi^0$  is the equilibrium single-particle density matrix, and  $\varphi^1$  is the small change induced by  $U$ . Since the self-consistent field vanishes in thermal equilibrium,  $\varphi^0$  is just the density matrix for noninteracting electrons in a uniform magnetic field. Linearizing Eq. (1) in  $U$  and  $\varphi^1$  gives:

$$i \dot{\varphi} = (H_0, \varphi^1) + (V + U, \varphi^0). \quad (2)$$

Equation (2) is to be solved subject to the boundary condition that  $\varphi^1$  vanishes at times before the perturbing field has been turned on.

Equation (2) can be solved exactly for the one-particle density matrix, in terms of which one can express the Fourier transform of the change

in the density of particles induced by  $U$ . Details of the calculation can be found in ref. (7) or (9). The result (in units where  $\hbar = 1$ ) is

$$\varrho^1(\mathbf{k}, \omega) = L(\mathbf{k}, \omega) U(\mathbf{k}, \omega), \quad (3)$$

where  $L$ , the linear response function, has the form

$$L(\mathbf{k}, \omega) = L^0(\mathbf{k}, \omega) / \left[ 1 - \frac{4\pi e^2}{k^2} L^0(\mathbf{k}, \omega) \right], \quad (4)$$

$$L^0(\mathbf{k}, \omega) = m\omega_c \sum_{nn'} \int \frac{dp}{(2\pi)^2} \frac{f_n(p - k_{||}/2) - f_{n'}(p + k_{||}/2)}{\omega - \frac{pk_{||}}{m} + (n - n')\omega_c} C_{nn'}(k_{\perp}), \quad (5)$$

$k_{||}$  and  $k_{\perp}$  are the components of  $\mathbf{k}$  parallel and perpendicular to the magnetic field, and  $\omega_c$  is the cyclotron frequency  $\omega_c = eH/mc$ . The coefficients  $C_{nn'}$  are given by the squared matrix element of the plane wave  $\exp(ik_{\perp}x)$  between two eigenstates of a one-dimensional oscillator with mass  $m$  and frequency  $\omega_c$ :

$$C_{nn'}(k_{\perp}) = |\langle n' | \exp(ik_{\perp}x) | n \rangle|^2.$$

For our analysis we shall only need the facts that  $C_{nn'}$  vanishes as

$$k_{\perp}^2 | n - n' |$$

as

$$k_{\perp} \rightarrow 0;$$

$$C_{n,n+1} \approx (n + 1) k_{\perp}^2 / 2m\omega_c;$$

and

$$C_{nn} \approx 1 - (n + \frac{1}{2}) k_{\perp}^2 / 2m\omega_c.$$

Finally,

$$\begin{aligned} f_n(p) &= 1 / (\exp [\beta(p^2/2m + n\omega_c - \mu)] + 1) \\ &\quad + 1 / (\exp [\beta(p^2/2m + (n + 1)\omega_c - \mu)] + 1), \end{aligned}$$

is a sum of Fermi functions for the two possible spin orientations.

The long wavelength resonances determined by the poles of  $L(\mathbf{k}, \omega)$  fall naturally into two classes. Two resonances persist in the limit of infinite wavelength. They involve motions resulting from a competition

between the Lorentz force and the tendency to execute plasma oscillations along the direction of propagation. When  $k$  is small but not zero there are additional modes with frequencies close to  $\pm n\omega_c$ , where  $n$  is an integer greater than or equal to 2. These are very weakly excited by long wavelength disturbances and undergo heavy Landau damping unless the direction of propagation is perpendicular to the magnetic field, or unless the temperature is very close to zero.

The frequencies of the first type of resonance are given to lowest order by the poles of  $L$  when  $k = 0$ . These occur at the roots  $\omega_{\pm}$ , of

$$1 = \frac{\omega_p^2 \cos^2 \theta}{\omega^2} + \frac{\omega_p^2 \sin^2 \theta}{\omega^2 - \omega_c^2},$$

where  $\theta$  is the angle between  $\mathbf{k}$  and  $\mathbf{H}$  and  $\omega_p$  is the plasma frequency,

$$\omega_p = 4\pi\varrho^0 e^2/m.$$

The residue of  $L$  at the positive roots  $\omega_{\pm}$  are

$$\mathbf{r}_{\pm} = \pm \frac{\varrho k^2}{2m} \frac{|\omega_{\pm}| (\omega_{\pm}^2 - \omega_c^2)}{\omega_p^2 (\omega_p^2 - \omega_{\pm}^2)},$$

and  $-r_{\pm}$  at the roots  $-\omega_{\pm}$ . In general when the linear response function is a sum of first order poles at  $\omega_i$  with residue  $r_i$ , the longitudinal sum rule,

$$\sum \mathbf{r}_i \omega_i = \varrho k^2/m,$$

is satisfied. In the present case the four poles at  $\pm \omega_{\pm}$  exhaust the sum rule as  $k \rightarrow 0$ .

These resonant frequencies are the same as those found by Gross in the long wavelength limit of the analogous classical problem. They have a rather simple interpretation, being just the normal frequencies of a single electron, moving in the magnetic field  $\mathbf{H}$ , and in a one-dimensional oscillator well along the direction of  $\mathbf{k}$ , with frequency  $\omega_p$ ; i.e., they are the eigenvalues of the one-electron equation:

$$-m\omega^2 \mathbf{r} = -m\omega_p^2 \hat{\mathbf{k}}(\hat{\mathbf{k}} \cdot \mathbf{r}) - i \frac{\omega e}{c} \mathbf{r} \times \mathbf{H}.$$

Belonging to the eigenvalue  $\omega_{\pm}$  of the one-electron problem, is a normal

mode in which the electron moves on an elliptical orbit in velocity space with axes proportional to

$$(\omega_c/\omega_{\pm}) (\hat{\mathbf{H}} \times \hat{\mathbf{k}})$$

and

$$\hat{\mathbf{k}} = (\omega_c/\omega_{\pm})^2 \hat{\mathbf{H}} (\hat{\mathbf{H}} \cdot \hat{\mathbf{k}}).$$

The behavior of such a single electron is helpful in visualizing the collective motion of the electron gas when semiclassical conditions hold — i.e., when the wavelength is long enough and the magnetic field weak enough to permit the calculation of a joint single-particle distribution function in position and velocity. Under these conditions the self-consistent field approximation enables one to calculate the time-dependent joint-distribution function by using the linearized Boltzmann-Vlasov equation, in which the initial equilibrium electronic distribution function is given by a Fermi distribution. From the solution of this equation one can show that at a long wavelength resonance, the collective motion is such that the velocity distribution at each point moves without distortion along the same orbit in velocity space as that belonging to the corresponding normal mode of the one-electron problem.

This analogy to the one-electron problem gives a simple picture of the collective motion in several limiting cases:

(a) Propagation parallel to  $\mathbf{H}$  ( $\sin \theta \approx 0$ ):

$$\omega_+^2 = \omega_p^2 \left[ 1 + \frac{\sin^2 \theta \omega_c^2}{\omega_p^2 - \omega_c^2} + O(\sin^4 \theta) \right],$$

$$\omega_-^2 = \omega_c^2 \left[ 1 - \frac{\sin^2 \theta \omega_p^2}{\omega_p^2 - \omega_c^2} + O(\sin^4 \theta) \right].$$

As  $\sin \theta \rightarrow 0$ , the mode belonging to  $\omega_+$  reduces to a linear plasma oscillation along the direction of  $\mathbf{k}$  and  $\mathbf{H}$ ; the other mode reduces to uniform circular motion about this direction with frequency  $\omega_c$ . When  $\sin \theta$  vanishes, the plasmon alone exhausts the sum rule, reflecting the impossibility of exciting a purely transverse motion by a longitudinal perturbation.

(b) Propagation perpendicular to  $\mathbf{H}$  ( $\cos \theta \approx 0$ ):

$$\omega_+^2 = \omega_p^2 + \omega_c^2 - \frac{\cos^2 \theta \omega_p^2 \omega_c^2}{\omega_p^2 + \omega_c^2} + 0(\cos^4 \theta),$$

$$\omega_-^2 = \frac{\omega_p^2 \omega_c^2 \cos^2 \theta}{\omega_p^2 + \omega_c^2} + 0(\cos^4 \theta).$$

As  $\cos \theta \rightarrow 0$  the  $\omega_-$  mode reduces to uniform translation parallel to  $\mathbf{H}$  and perpendicular to  $\mathbf{k}$ , and its relative contribution to the sum rule vanishes. The dominant mode belongs to  $\omega_+$ , and involves an elliptical motion in the plane perpendicular to  $\mathbf{H}$ , with axis parallel to  $\mathbf{k}$  being greater than the perpendicular axis by a factor

$$(1 + \omega_p^2/\omega_c^2)^{1/2}.$$

(c) Weak magnetic field or high density ( $\omega_p^2 \gg \omega_c^2$ ):

$$\omega_+^2 = \omega_p^2 [1 + \sin^2 \theta (\omega_c/\omega_p)^2 + 0(\omega_c/\omega_p)^4],$$

$$\omega_-^2 = \omega_c^2 \cos^2 \theta [1 + 0(\omega_c/\omega_p)^2].$$

The mode  $\omega_-$  is what one would find by ignoring the component of  $\mathbf{H}$  perpendicular to  $\mathbf{k}$  and applying case (a); this is because the strong coulomb interaction leads to a rigidity against low-frequency long-wavelength longitudinal oscillations, and hence suppresses precession about the component of  $\mathbf{H}$  perpendicular to  $\mathbf{k}$ . The other root is essentially the plasmon; the way in which it is modified by the weak magnetic field is just what one would find by ignoring the component of  $\mathbf{H}$  parallel to  $\mathbf{k}$  and applying case (b). The plasmon again dominates the sum rule, since

$$\mathbf{r}_-/\mathbf{r}_+ \approx (\omega_c/\omega_p)^3 \cos \theta \sin^2 \theta.$$

(d) Strong magnetic field or low density ( $\omega_c^2 \gg \omega_p^2$ ):

$$\omega_+^2 = \omega_c^2 [1 + \sin^2 \theta (\omega_p/\omega_c)^2 + 0(\omega_p/\omega_c)^4],$$

$$\omega_-^2 = \omega_p^2 \cos^2 \theta [1 + 0(\omega_p/\omega_c)^2].$$

The root  $\omega_-$  can be regarded as a plasmon in which, because of the strong magnetic field, the particles move parallel to  $\mathbf{H}$  instead of  $\mathbf{k}$ . The other root is essentially the unperturbed cyclotron resonance; the weak coulomb interaction changes the circular orbit about  $\mathbf{H}$  to an elliptical orbit perpendicular to  $\mathbf{H}$  with minor axis perpendicular to  $\mathbf{k}$ . The oblique plasmon still dominates the sum rule, since

$$\mathbf{r}_+/\mathbf{r}_- \approx (\omega_p/\omega_c) (\sin^2 \theta/\cos \theta).$$

Effects which are not classical first appear in the lowest order  $\mathbf{k}$  dependent terms of the resonant frequencies. Quantum effects arise here because these terms depend on the mean equilibrium energy of an electron in a magnetic field. When orbit quantization becomes important this energy will develop an oscillatory dependence on the magnetic field. These oscillations are, however, small corrections to the much larger contributions to the energy which are independent of and linear in  $\mathbf{H}$ , and should therefore be very hard to observe.

Another effect which arises when  $\mathbf{k} \neq 0$  is the familiar Landau damping, which occurs when it is possible for the collective mode to give up its energy and momentum by exciting an electron to a higher state. In the absence of a magnetic field Landau damping of the plasmon is small, because in order for a particle to absorb the energy  $\omega_p$  and the small momentum  $\mathbf{k}$ , it must have a very large initial momentum, and is therefore unlikely to be available at low temperatures. In a magnetic field, however, only the momentum parallel to  $\mathbf{H}$  must be conserved. A collective state with  $\omega \gg \omega_c$ , can give up the bulk of its energy by exciting an electron to a level with higher oscillator quantum number  $n$ , leaving only a small remainder to be absorbed by a change in the electron's momentum parallel to  $\mathbf{H}$ . The initial momentum parallel to  $\mathbf{H}$  that such a particle must have is therefore enormously reduced, and the probability of its being available correspondingly enhanced. In the limit of small  $\mathbf{k}$  these factors giving the density of available particles more than outweigh the dynamical transition probabilities in determining the size of the lifetime. One can therefore conclude that a magnetic field increases the Landau damping of the plasmon-like modes.

This feature of the Landau damping becomes very important in the case of the weakly excited higher order cyclotron resonances, occurring

very close to  $\pm n\omega_c$ . Because all but a minute part of their energy can be absorbed by excitation of an electron to a higher oscillator level, there will be many electrons available to absorb their momentum parallel to  $\mathbf{H}$  while taking up the very small remaining energy, unless the wave carries no momentum parallel to  $\mathbf{H}$ . Their Landau damping is therefore very large at nonzero temperatures, unless  $\mathbf{k}$  is perpendicular to  $\mathbf{H}$ . Their behavior in the two cases in which they do not undergo severe Landau damping — perpendicular propagation and zero temperature — is quite different.

### A. PERPENDICULAR PROPAGATION

When  $k_{||}$  is zero and  $k_1$  is small, resonances occur at energies  $\omega_n$  very close to  $n\omega_c$ , for  $|n| \geq 2$ . It can be shown that the amount by which  $\omega_n$  differs from  $n\omega_c$  is proportional to  $k^{2n-1}$ ; the magnitude of  $\omega_n$  exceeds  $|n\omega_c|$  if  $|n\omega_c| > (\omega_p^2 + \omega_c^2)^{1/2}$ ; otherwise it is less than  $|n\omega_c|$ . The residue at the  $n$ th higher order cyclotron resonance vanishes as  $k^{2n}$ , and they are therefore progressively more difficult to excite. The Boltzmann-Vlasov equation furnishes a picture of the collective motions associated with these resonances in the semiclassical case. At a given time the local velocity distribution has the following structure: its (spherically symmetric) equilibrium value is enhanced in  $n$  directions perpendicular to  $\mathbf{H}$  spaced  $2\pi/n$  apart, and diminished in between these directions. As time evolves this distorted velocity distribution rotates about the direction of  $\mathbf{H}$  with frequency  $\omega_c$ . This behavior can be understood as arising from  $n$  separate groups of electrons, all undergoing ordinary cyclotron motions with frequency  $\omega_c$ , but so arranged that at any given point of space the density goes through a maximum and minimum  $n$  times in a single period.

### B. ZERO TEMPERATURE

In a fixed magnetic field, as  $\mathbf{k}$  approaches zero, undamped higher order cyclotron resonances occur in the response function for arbitrary directions of propagation. When  $\mathbf{k}$  is perpendicular to  $\mathbf{H}$  their wavelength dependence is as described above, but for any other direction of

propagation their behavior is quite different for sufficiently small  $\mathbf{k}$ . The analysis one goes through to derive the properties of these resonances from Eq. (5) is quite similar to the usual RPA derivations of zero sound. One finds that for small  $k$  resonances occur at  $\pm \omega_n$ , where

$$\omega_n = n\omega_c + |\mathbf{k}V_F \cos \theta|, \quad n \geq 2, \quad V_F = (2\mu/m)^{1/2},$$

when  $|n\omega_c|$  exceeds the two long-wavelength resonant frequencies  $|\omega_{\pm}|$ , and otherwise at

$$\omega_n = n\omega_c - |\mathbf{k}V_F \cos \theta|.$$

In a magnetic field the Fermi velocity,  $v_F$  is defined only along directions parallel to  $\mathbf{H}$ . The magnitude of the group velocity of these resonances is therefore given by the projection of the Fermi velocity on  $\mathbf{k}$ ; the group velocity has a positive component along  $\mathbf{H}$  when  $|n\omega_c| > |\omega_{\pm}|$ , and a negative component otherwise.

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# **Temperature-Dependent Random Phase Approximations for the Heisenberg Ferromagnet**

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## **I. Introduction**

In recent years some new approximations have been developed to the statistical mechanics of the Heisenberg ferromagnet based on analogy or application of current many-body methods. The variant versions of the temperature-dependent random phase approximation (RPA) at low temperatures yield the collective spin excitations, the spin waves, or magnons, and in the vicinity of  $T_c$ , the Curie temperature, give a correction to the Weiss molecular field approximation (MF). We shall describe the general nature of these approximations and subsequently develop many of the results by means of the method of approximate decoupling of the equations of motion. In particular we shall consider the resolution of the disagreement which had existed in regard to the corrections to the spin wave contributions at low temperatures between the original version of the RPA calculations (1) and the results of Dyson (2). Further we shall examine the question of the behavior of the RPA results above  $T_c$  and the relation of this question to the characterization of the high temperature limit of the RPA as a high density expansion (3), an expansion in  $1/z^*$ ,  $z^*$  being the effective number of interacting spins.

The great progress in recent years in the understanding and calculation of the properties of many-particle systems has centered in two factors. There is often a relatively simple low-lying excitation spectrum even

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in strongly interacting many-body systems, comprising a few types of rather well-defined excitations, some single-particle-like (quasi particles) and some of a collective nature which at sufficiently low temperatures can be regarded as a dilute gas of weakly interacting particles. Secondly, the ground state, the low excitations and their interactions can be obtained in various model situations such as low density, high density, or bound state models such as B.C.S.-Bogolyubov for superconductivity, by means of diagram summation, equations of motion methods, Green's function methods, etc. With the ground-state and low-lying excitation spectrum known, one can also obtain for low temperatures the equilibrium thermodynamics properties as well as transport properties.

For the Heisenberg ferromagnet results of this nature had already been established in some detail by Dyson (2) some years ago. The ground state is obtained trivially, comprising the state with all spins aligned in the direction opposite to some orienting field (the electron charge being negative). The calculation of the leading term of the noninteracting spin wave spectrum was obtained by F. Bloch in 1930. It was not until the work of Dyson that it was established that at low temperatures spin wave interactions are weak; that up to the order of terms exponential in  $(-T_c/T)$  the excitations can be regarded as weakly interacting boson gas. Thus the contributions to an expansion in temperature arise from the spin waves and from interaction terms involving scattering of the spin waves, regarded as bosons, this interaction called by Dyson the dynamical interaction; the effects due to the nonboson character of the spin excitations (the kinematical interaction) contributing only exponentially. The magnetization has, according to Dyson, an expansion of the form

$$\begin{aligned} M(T) = M(0) + A_1 T^{3/2} + A_2 T^{5/2} + \dots + B_1 T^4 + \dots \\ + O[\exp(-aT_c/T)] \end{aligned} \quad (1)$$

where then term in  $T^4$  is the leading effect of the dynamical interaction. Dyson did not evaluate the kinematical correction and his methods cannot be readily extended to treat the region of  $T_c$  where this correction certainly becomes important. In the problem of ferromagnetism there is considerable interest in the region of  $T_c$  and above.

Although we will be discussing the model problem, only a few remarks

at least should be made as to the conditions of validity of the model. We are denoting by the name Heisenberg ferromagnet that model of the ferromagnet obtained for the spin Hamiltonian

$$H = - \sum_{i < j} 2J_{ij} S_i \cdot S_j + h \sum_j S_j^z \quad (2)$$

when the interaction  $J_{ij}$  between spin of magnitude  $S$  at sites  $(i, j)$  is positive over sufficient domain that the ground state has all spins aligned along the direction opposite the orienting field specifying the  $z$  direction. The original idea which provided the basis for such a Hamiltonian was generalization for the crystal of a Heitler-London type calculation of the  $H_2$  molecule. This suggestion of Heisenberg and Frenckel was that ferromagnetism has its origin in the ordering of the uncompensated spins in the unfilled (inner)  $d$ -shell brought about by correlation through the Pauli exclusion principle, the  $J_{ij}$  being taken to be the exchange integrals between  $d$ -electrons localized on nearby sites. The validity of this type of picture depends on such questions as the degree of localization the  $d$ -electrons, whether even sufficiently localized electrons would lead to such a Hamiltonian with the possibility of either sign (not all transition metals being ferromagnetic), and even with the above conditions satisfied whether the magnitude is great enough to account for observed  $T_c$ . In the above form the Heisenberg-Frenckel model is evidently wrong and in any case certainly incomplete. For transition metals the detailed origin of the magnetically ordered states remains an open question, while for rare earths, the interaction between inner shell  $f$ -electrons and conduction electrons including at least a substantial  $f$ -conduction electron exchange integral leads to a spin Hamiltonian of the above type. In any case the spin Hamiltonian gives an ordered ground state found in real ferromagnets, and gives a spin wave type excitation which is evidently found even in transition metals. One can then accept the Heisenberg model in the form of the above spin Hamiltonian as a qualitatively reasonable though still largely phenomenological model for the ordered magnetic properties of ferromagnetics, metals included, the detailed accuracy being uncertain.

In attempting to go beyond the low-temperature properties of a ferromagnet a variety of approximations have been developed through the years. First and foremost of these was the MF, in which the interaction

of a given spin with its neighbors is replaced by an average interaction determined self-consistently. This approximation gives a qualitatively reasonable description of the properties of the ferromagnet including the value of  $T_c$ , and can also readily be applied to other types of magnetic ordering, such as antiferromagnetism, etc. MF can be shown to be exact in the limit of infinite range and infinitesimally weak interactions. There are, however, two distinct limitations to this approximation:

- (i) MF is wrong at low temperatures as it does not include spin waves.
- (ii) Above  $T_c$  the results are qualitatively wrong as MF does not exhibit the short-range order effects observed in real ferromagnets.

Above  $T_c$  series expansions in  $1/T$  have been examined in detail and the results extrapolated to the Curie temperature (4). These methods seem to lead to the most accurate characterization known of  $T_c$  and of the nature of the phase transition. Since the validity of the spin Hamiltonian is open to question, these results provide the best available test of high-temperature behavior aside from internal consistency.

There also exist a series of approximations which we might call small-cluster approximations (5) which attempt to generalize the method of the MF in the sense of treating exactly the explicit interactions of some small group of spins and the interactions with the rest by some self-consistency criterion. These methods correct MF results to the extent of adding short-range order effects above  $T_c$ . They do not, however, treat low temperatures any better and in addition have no particular criterion of validity. Some work on such methods in analogy with the low-density type approximation (6) of many-body theory has been carried out. In the case of a dilute alloy this type of expansion should lead in fact to a low-density expansion which may be valid.

The application of a temperature-dependent RPA to the spin Hamiltonian leads to the spin wave approximation as  $T \rightarrow 0$  and to the spherical model (7) above  $T_c$ , this latter being a mathematical model in which the discrete spin components are replaced by continuous variables subject to the constraint that the value of total spin is fixed. The RPA approach was originally developed by Tyablikov (1) by a Green's function decoupling method and by F. Englert (1) by the Kubo formalism. Brout's (3) analysis of the problem implied that the high-temperature region

was a high-density expansion. Two problems arose with respect to this approximation; the more extensively discussed was the  $T^3$  correction to spin wave results in disagreement with Dyson, while the second of perhaps greater consequence is the question of the inadequacy of the treatment of the transition region. Attempts to resolve the first question produced a spurt of activity reproducing Dyson's results in a variety of ways (8) most of which assumed one feature or another of Dyson's results to begin with. Among these one of the more interesting is the work of Keffer and Loudon (8) which suggest a physical interpretation of the Dyson correction leading to an energy renormalization of the spin wave frequency instead of the magnetization renormalization found by RPA. Just where RPA goes wrong has been shown in various ways; for example, a diagrammatic expansion shows how the  $T^3$  correction of the kinematical interaction is cancelled to yield  $T^4$ . Having understood the origin of the discrepancy and especially since an argument can be given whereby the kinematical interaction may become as important as the dynamical before the discrimination between the  $T^3$  and  $T^4$  for a long-range interaction, one might suppose the RPA result to be fairly good. That this is open to question is a consequence of the second difficulty, the treatment of the transition region. An analysis (9) of the region of the Curie temperature shows a spurious first-order phase transition, the usual transition occurring for a finite magnetic field. The diagram derivations of this result show a formal discrepancy which seems extremely difficult to eliminate. To what extent the high-density expansion remains valid down to  $T_c$  or how to define it so that it does is unclear. Attempts to find improved approximations of this sort through the whole temperature range not having the difficulties of RPA have not been wholly successful. The best of these is probably that of Callen (10) using the Bogolyubov-Tyablikov (11) Green's function decoupling method. Decoupling in such a way that he interpolates between a low-temperature energy renormalization of the spin wave frequency and a high-temperature magnetization renormalization (a result suggested by various arguments), Callen finds a low temperature correction proportional to  $T^4$  with a spurious  $T^{(3/2)(2S+1)}$ . Thus only for spin  $\frac{1}{2}$  does the spurious  $T^3$  persist for spin 1; it is  $T^{9/2}$  which is negligible. The behavior in the transition region has not been thoroughly explored but the Curie temperature obtained is a distinct improvement over the spherical model result.

As for the simplest way to illustrate many of the aspects of the RPA results (12) and perhaps the best to exhibit the approximation in its various elements, we shall develop RPA via the equations of motion method (13). Direct application of RPA at zero temperature gives the spin wave results; while a direct finite temperature RPA give the results of Tyablikov (1) and Englert (1). RPA plus the boson approximation (i.e., neglect of kinematical interaction) yields Dyson's results in a form analogous to that found by Keffer and Loudon, agreeing up to the first Born approximation of the  $T^4$  coefficient. Callen's results for spin  $\frac{1}{2}$  are also readily obtained by this method. This series of results eliminates the question of the relation of the low-temperature excitations to approximations extending to and above  $T_c$ , by means of some approximation to the kinematical interaction. Inclusion of the kinematical interaction through approximate, temperature-dependent commutation relations is to begin with somewhat arbitrary. A connection is then made with the  $1/z^*$  expansion for temperatures greater than  $T_c$ . The difficulties of the  $1/z^*$  expansion near the Curie temperature concludes the discussion.

## II. Equations of Motion for Heisenberg Ferromagnet

In this section are set up the equations of motion for the Heisenberg ferromagnet. In the following section, by approximately decoupling the equations of motion by means of different versions of RPA typical results are obtained by a variety of other methods and then these results are summarized and discussed. The use of RPA to decouple the equations of motion has the advantage of yielding in a relatively simple way most of the interesting results and displaying many of the factors of interest in their analysis.

For a system of  $N$  spin of magnitude  $S$  on a periodic lattice with an external magnetic field in the  $z$  direction  $h$  (in units of  $g\mu_0$ ,  $g$  being the spectroscopic splitting factor and  $\mu_0 > 0$  the Bohr magneton), the Hamiltonian for the Heisenberg ferromagnet being given by Eq. (2) where the "exchange integral"  $J_{ij}$  extends over some range  $r_0$  much less than crystal dimensions, and  $J > 0$  corresponds to a ferromagnetic ground state with all spins aligned in the  $-z$  direction. Introducing the Fourier analysis of  $S_j$  and of  $J_{ij}$  we obtain

$$H = -2 \sum_q J(q) (S_q^z S_{-q}^z + S_q^+ S_{-q}^-) + N^{1/2} S_0^z h \quad (3)$$

where

$$S_q = N^{-1/2} \sum_j \exp(-iq \cdot r_j) S_j \quad (4)$$

and

$$J(q) = \sum_j J_{ij} \exp[iq \cdot (r_i - r_j)] = N^{-1/2} \sum_{ij} J_{ij} \exp[iq \cdot (r_i - r_j)]. \quad (5)$$

The spin operators  $S_q^\pm$  and  $S_q^z$  have the commutation relations (taking  $\hbar = 1$ )

$$\begin{aligned} [S_q^+, S_{q'}^-] &= 2N^{-1/2} S_{q+q'}^z \\ [S_q^z, S_{q'}^\pm] &= \pm N^{-1/2} S_{q+q'}^\pm \end{aligned} \quad (6)$$

obtained by Fourier transforming the usual spin commutation relations

$$\begin{aligned} [S_i^+, S_j^-] &= 2S_i^z \delta_{ij} \\ [S_i^z, S_j^\pm] &= \pm \delta_{ij} S_j^\pm. \end{aligned} \quad (7)$$

By use of the commutation relation (6), the assumed inversion symmetry  $J(q) = J(-q)$  and  $\sum_q J(q) = 0$ , we find the equations of motion

$$-iS_{q_1}^+ = [H, S_{q_1}^+] = 2N^{-1/2} \sum_q [J(q) - J(q_1 - q)] S_q^+ S_{q_1-q}^z + hS_{q_1}^+. \quad (8)$$

This generator  $S_q^+$  acting on the ground state  $|0\rangle$  is the appropriate spin wave variable since

$$[H, S_{q_1}^+] |0\rangle = [h + 2J(0)S - 2J(q)S] S_{q_1}^+ |0\rangle \quad (9)$$

and hence  $S_{q_1}^+ |0\rangle$  is an exact eigenstate with energy

$$\omega_0(q_1) = \hbar + 2[J(0) - J(q)]S \quad (10)$$

for this state

$$\sum_j S_j^z S_{q_1}^+ |0\rangle = (NS - 1) S_{q_1}^+ |0\rangle. \quad (11)$$

Actually of much more significance than that a single spin wave state generated by  $S_q^+$  is an exact eigenstate is the fact that multiple spin wave states generated by operating on the ground state with two or more  $S_{q_i}^+$  operators yield weakly interacting states at low temperatures.

The straightforward evaluation of RPA would be to take  $q = q'$

and then average  $S^z$  in the ground state, or in a thermal average. This is, however, not a well-defined procedure since

(i)  $\langle S_q^z \rangle$  may be variously defined in approximately decoupling the equations of motion for  $S_q$ : —  $iS_{q_i}^+ \approx \omega(q_i) S_{q_i}^-$ . For spin  $\frac{1}{2}$  we can write an appropriate identity for  $S^z$  in terms of the operators  $S^+S^-$ ; for spin greater than  $\frac{1}{2}$  such identities introduce  $(S^z)^2$  so that the results are again not completely defined by our equations. To obtain a particular approximation we then require a choice of operator relationship between  $S^z$  in terms of the transverse spin operators and then decouple the equations of motion taking averages of  $S^+S^-$ ; the results are then defined self-consistently.

(ii) The evaluation of these self-consistent averages, however, remains very difficult in view of the nonorthogonality of this representation in states  $\Pi(S_{q_i}^+) | n \rangle | 0 \rangle$  being nonorthogonal. By further approximating the commutation relations

$$[S_{-q}^-, S_q^+] \simeq \langle | S_q^z | \rangle \delta_{q,q'} \quad (12)$$

then

$$\langle S_q^+ S_{-q}^- \rangle = 2 \langle | S^z | \rangle \varphi(q) \quad (13)$$

with

$$\varphi(q) = \{\exp \beta [\omega(q) + h] - 1\}^{-1}. \quad (14)$$

However,  $\langle | S^z | \rangle$  introduced here need not necessarily be the same quantity as obtained by averaging the operator expression introduced in (i) above. In fact at low temperatures we obtain Dyson's results by taking the approximation  $\langle | S^z | \rangle = 2S$  in Eq. (12), while we take  $S_1^z = -S + S_1^+S_1^-$  in the equations of motion and average this self-consistently to obtain the magnetization. The first approximation corresponds to the neglect of the kinematical interaction, while the second leads to the correct dynamical interactions. It is clear from this discussion that this is a subtle point and this point of view does not lead naturally to Dyson's results without further consideration.

### III. Low Temperature Results

The low-temperature properties of the Heisenberg ferromagnet (2, 8) will now be obtained by the use of RPA assuming Dyson's proof that

for low-temperature properties, the excitations of the Heisenberg ferromagnet can be treated as a weakly interacting dilute boson gas. In that case the energy of a spin wave is given by

$$\omega(q) = \omega_0(q) + t(q) \quad (15)$$

where  $\omega_0(q)$  is the unperturbed spin wave energy [Eq. (10)] and  $t(q)$  is the forward-scattering amplitude in matter. Since the interaction has no singularities (at low  $T$ ) and is weak, the first Born approximation to  $t(q)$  is already a good approximation. In order to relate to higher temperature results as well as to indicate by a unified method the approximations involved, we also use RPA to obtain results for low temperatures. In this way the magnetization is found to have a leading correction to the noninteracting spin wave result a term proportional to  $T^4$ ; the  $T^4$  coefficient agreeing with Dyson's result with  $t(q)$  approximated by the first Born approximation. By use of higher RPA approximations even more accurate results could be obtained, but this will suffice.

In Eq. (8) we have written the equations of motion for the operator  $S_q^+$ . Acting on the ground state  $S_q^+$  produced an exact eigenstate [Eq. (9)], a spin wave state corresponding to the propagation of a single reversed spin through the lattice with wave number  $q$ . Let us consider matrix elements in the nonorthogonal representation of products of the  $S_q^+$  on the ground state. There then result two types of interaction effects for the spin waves: that due to the nonorthogonality of the representation Dyson termed the kinematical interaction, while that involving off-diagonal matrix elements of the Hamiltonian he termed the dynamical interaction. In demonstrating that the kinematical interaction contributes only to order  $\exp(-aT_c/T)$  [ $a$  is  $O(1)$ ], Dyson showed that the kinematical interaction is negligible at low temperatures. On the other hand it certainly becomes important near the Curie temperature and due to the weakness of the dynamical interaction which is negligible until  $T/T_c \sim \frac{1}{3}$ , it is not at all clear that the kinematical term may not begin to be of importance; especially is this true for long-range interactions. In any case for low temperatures we shall assume with Dyson that we can neglect the kinematical interaction. This can be done by replacing the equations of motion for the  $S_q^+$  by an equivalent problem in terms of boson operators for which a Hamiltonian having the same diagonal and off-diagonal matrix elements in an independent boson representation

as does the spin Hamiltonian in the spin wave representation. This is then equivalent to neglecting the kinematical while retaining the dynamical interaction. We then linearize the equations of motion and average the operators; this yields the RPA results for low temperatures.

Noting that

$$[(H, S_{q_1}^+), S_{q_2}^+] = 2N^{-1} \sum_q \{J(q) - J(q_1 - q)\} S_q^+ S_{q_1+q_2-q}^+ \quad (16)$$

which can be written in the more symmetrical form

$$[(H, S_{q_1}^+), S_{q_2}^+] = \frac{1}{N} \sum_q \Gamma_{q_1 q_2}^q S_{q_1-q}^+ S_{q_2+q}^+ \quad (17)$$

$$\Gamma_{q_1 q_2}^q \equiv [J(q_1 - q) + J(q_2 + q) - J(q) - J(q_1 - q_2 - q)]$$

further commutators with  $S_q^+$ , being zero. Then we can evaluate  $H$  acting on a state  $|a\rangle = \Pi_i (S_{q_i}^+)^{n_i} |0\rangle$  by bringing  $H$  to the right and taking commutators; using Eq. (8) and (17) we obtain

$$H|a\rangle = \{E_0 + \sum_i [h + \omega_0(q_i)] n_i\} |a\rangle + \frac{1}{N} \sum_q \sum_{q_1} \sum_{q_2} \Gamma_{q_1 q_2}^q |b\rangle \quad (18)$$

$$E_0 = -N(J_0 S^2 + hS) \quad (19)$$

where  $|b\rangle$  is a state differing from  $|a\rangle$  by the replacement of the spin wave pair  $(q_1, q_2)$  by the pair  $(q_1 - q, q_2 + q)$ . Introducing a set of boson states

$$|a\rangle = \Pi (b_{q_i}^+)^{n_i} |0\rangle \quad (20)$$

for all  $n_i$  and a corresponding boson Hamiltonian  $H'_i$  which we need not even write explicitly, we require

$$H|a\rangle = E_0|a\rangle + \sum_i [\omega_0(q_i)] n_i |a\rangle + N^{-1} \sum_q \sum_{q_1} \sum_{q_2} \Gamma_{q_1 q_2}^q |b\rangle \quad (21)$$

with the operators,  $b_q, b_q^+$  obeying boson commutation relations

$$[b_q, b_{q'}^+] = \delta_{qq'} \quad (22)$$

and state  $|b\rangle$  differing from  $|a\rangle$  by the presence of the pair of states  $(q_1, -q, q_2 + q)$  in place of  $(q_1, q_2)$ . We can obtain this by replacing in

the equation of motion for the spin operators

$$\begin{aligned} S_q^+ &\rightarrow b_q^+ \\ S_{-q'}^- &\rightarrow b_{q'}^- \\ S_q^z &\rightarrow -N^{1/2} S \delta_{q,0} + N^{-1/2} \sum_{q'} b_{q+q'}^+ b_{q'}^- . \end{aligned} \quad (23)$$

This is equivalent to writing

$$S_q^z = N^{1/2} S \delta_{q,0} + N^{-1/2} \sum_{q'} S_{q+q'}^+ S_{-q'}^- / 2S \quad (24)$$

and approximating the spin commutators

$$[S_{-q'}, S_q^+] = 2S \delta_{q,q'} . \quad (25)$$

Then corresponding to the equations of motion (8) we obtain

$$[\mathbf{H}', b_{q_1}^+] = [\omega_0(q_1) + h] b_{q_1}^+ - N^{-1} \sum_q [J(q) - J(q_1 - q)] b_q^+ b_{q_1+q'-q}^- b_{q'}^- \quad (26)$$

and instead of (17) we have

$$[(H, b_{q_1}^+), b_{q_2}^+] = N^{-1} \sum_q I_{q_1 q_2}^q b_{q_1-q}^+ b_{q_2+q}^+ \quad (27)$$

from these two equations Eq. (20) follows.

Linearizing Eq. (26) and averaging the coefficient we have two terms, equivalent to a temperature-dependent Hartree-Fock approximation. The direct term ( $q_1 = q$ ) alone leads to the  $T^3$  correction to the magnetization found by the original RPA methods, this being cancelled to leading order by the exchange term ( $q' = q$ ) leaving the  $T^4$  dependence. We obtain

$$\omega(q) = \omega_0(q) + N^{-1} \sum_{q'} I_{qq'}^0 \langle b_{q'}^+, b_{q'}^- \rangle \quad (28)$$

where self-consistently

$$\langle b_{q'}^+, b_{q'}^- \rangle = \varphi(q') = \{\exp \beta [\omega(q') + h] - 1\}^{-1} . \quad (29)$$

For low temperatures results are dominated by the long wavelength limit for which we can write for an isotropic crystal

$$\omega_0(q) = \alpha_1 q^2 + \alpha_2 q^4 + \dots \quad (30)$$

while

$$I_{qq'}^0 = \gamma q^2 q'^2 + O(q^6). \quad (31)$$

Summarizing the thermodynamic results for the ferromagnet: The magnetization is of the form [cf. Eq. (11)]

$$\begin{aligned} M(T) &= g\mu_0 \langle S^z \rangle \equiv -g\mu_0 S + N^{-1} \sum_{q'} \varphi(q') \\ &= -g\mu_0 S + A_1 T^{3/2} + A_2 T^{5/2} + \dots + B_1 T^4. \end{aligned} \quad (32)$$

The energy is of the form

$$E(T) = E_0 + \sum_q \omega(q) \varphi(q) = E_0 + D_1 T^{5/2} + D_2 T^{7/2} + \dots + E_1 T^5 \quad (33)$$

where we have used

$$\sum_q \varphi_0(q) = \sum_q \frac{1}{\exp[\beta\omega_0(q)] - 1} = A_1 T^{3/2} + A_2 T^{5/2} + \dots \quad (34)$$

and in the long wavelength limit

$$\omega(q) \cong A q^2 [1 + \sum q'^2 \varphi(q')] \approx A'(T) q^2 \quad (35)$$

$$A'(T) \approx A(1 + CT^{5/2}) \quad (36)$$

which is in the form of a frequency renormalization proportional to the leading term in the energy.

#### IV. High Temperature Results

We now extend RPA results to and above the Curie temperature by crudely including the kinematical interaction through temperature-dependent approximation to the commutation relations (9). The two approximations we will develop here will be carried out for spin  $\frac{1}{2}$  only. The first is equivalent to the original RPA results of Tyablikov (1) and Englert (1). The second approximation will be that of Callen (11).

Decoupling the equations of motions (8) by taking a thermal average of  $S_z$  we obtain

$$[H, S_{q_1}^+] = \{2[J(0) - J(q_1)] \langle |S^z| \rangle + h\} S_{q_1}^+ \quad (37)$$

where

$$\langle | S^z | \rangle = \langle -N^{-1/2} S_0^z \rangle = \langle -N^{-1} \sum_i S_i^z \rangle \quad (38)$$

and where we write [cf. Eq. (37) and (10)].

$$\omega_1(q) = \omega_0(q) \langle | S^z | \rangle / S. \quad (39)$$

For spin  $\frac{1}{2}$  we can write (14)

$$S_i^z = -\frac{1}{2} + S_i^+ S_i^- \quad (40)$$

and the Fourier transform is

$$S_q^z = -\frac{1}{2} N^{1/2} \delta_{q,0} + N^{-1/2} \sum_{q'} S_{q+q'}^+ S_{-q'}^- . \quad (41)$$

Approximating the commutation relations by

$$[S_{-q'}, S_q^+] = 2 \langle | S_0^z | \rangle \delta_{q,q'} \quad (42)$$

we then have

$$\langle S_q^+ S_{-q}^- \rangle = 2 \langle | S^z | \rangle \varphi_1(q) \quad (43)$$

with

$$\varphi_1(q) = \{\exp[\beta(\omega_1(q) + h) - 1]\}^{-1} \quad (44)$$

$\langle | S_q^z | \rangle$  is then determined self-consistently by averaging Eq. (41)

$$\langle | S^z | \rangle = \frac{1}{2} - 2 \langle | S^z | \rangle \Phi_1 \quad (45)$$

where we define  $\Phi_1$  by

$$\Phi_1 = N^{-1} \sum_q \varphi_1(q) . \quad (46)$$

At low temperatures the deviation from noninteracting spin wave behavior arises from the factor  $\langle | S^z | \rangle$  multiplying the boson distribution  $\varphi_1(q)$  from Eq. (43) for  $\langle S_q^+ S_{-q}^- \rangle$  and renormalizing the spin wave frequency [Eq. (35)]. The leading temperature dependence of  $\langle | S^z | \rangle$  being proportional to  $T^{3/2}$  we are led to the  $T^3$  correction to the magnetization.

To examine the high-temperature behavior we consider the limit  $h$  and  $\langle | S^z | \rangle$  going to zero. Since above  $T_c$  in our units  $\chi$  the susceptibility is determined by the equation

$$\frac{\langle | S^z | \rangle}{h} = \frac{\chi}{(g\mu_0)^2} \quad (47)$$

the Eq. (43) becomes

$$\lim_{n \rightarrow 0} \langle S_q^+ S_{-q}^- \rangle = \frac{2 \langle |S_z| \rangle}{2\beta[J(0) - J(q)] \langle |S_z| \rangle + h} \quad (48)$$

which is, using Eq. (47),

$$\lim_{n \rightarrow 0} \langle S_q^+ S_{-q}^- \rangle = \frac{2}{2\beta[J(0) - J(q)] + (g\mu_0)^2 \chi^{-1}}. \quad (49)$$

Similarly, Eq. (45) becomes

$$1 = N^{-1} \sum_q \frac{1}{\frac{1}{2} \beta[J(0) - J(q)] + (g\mu_0/2)^2 \chi^{-1}} \quad (50)$$

which determines  $\chi$ . To relate this to the spherical model we define  $\delta$  by

$$\chi^{-1} (g\mu_0/2)^2 = 1 - \frac{1}{2} \beta[J(0) - \delta] \quad (51)$$

and  $\delta$  is determined by the spherical model equation

$$1 = N^{-1} \sum_q \frac{1}{1 - \beta[J(q) - \delta]^{1/2}} \quad (52)$$

or equivalently

$$\delta = N^{-1} \sum_q \frac{J(q)}{1 - \beta[J(q) - \delta]^{1/2}}. \quad (53)$$

Writing the energy of the transverse operators in the Hamiltonian (Eq. 3) and using Eq. (48) we have

$$E_T = \frac{1}{N} \sum_q 2J(q) \langle S_q^+ S_{-q}^- \rangle = 2\delta. \quad (54)$$

The Curie temperature is then determined as the temperature where  $\chi^{-1}$  is zero

$$1 - \frac{1}{2} \beta_c(J_0 - \delta) = 0 \quad (55)$$

and on inserting this into Eq. (53) we find that

$$\frac{1}{2} \beta_c J_0 = F(1) \quad (56)$$

where

$$F(x) = \frac{1}{N} \sum_q \frac{1}{x - J(q)/J(0)} \quad (57)$$

which function has been evaluated for nearest neighbors for various lattices.

Callen's results obtained by use of Green's function methods can readily be derived by equations of motion for the case of spin  $\frac{1}{2}$ . Having done this we will give the results for arbitrary spin. We remark with Callen that the choice of Eq. (40) to express  $S^z$  in terms of the transverse spin operators is only one of several possible choices. One could, for example, choose instead

$$S_i^z = \frac{1}{2} (S_i^+ S_i^- - S_i^- S_i^+). \quad (58)$$

If we choose the relation so that the operators approximated have small average values, then at low temperatures since  $S^z \approx -S$  and  $(S^+ S^-)$  is a small quantity, we see why that choice was appropriate. On the other hand near  $T_c$ ,  $S_z \approx 0$  and hence both  $(S^+ S^-)$  and  $(S^- S^+)$  are small; in that case the choice of Eq. (58) might be expected to be appropriate. Choosing a linear combination with a coefficient  $\alpha$  chosen to interpolate between the two regions we have

$$S_i^z = \alpha(-\frac{1}{2} + S_i^+ S_i^-) + (1 - \alpha) \frac{1}{2} (S_i^+ S_i^- - S_i^- S_i^+) \quad (59)$$

with

$$\alpha = 2 \langle |S^z| \rangle \quad (60)$$

an appropriate choice since  $\alpha = 1$  at low temperatures and  $\alpha = 0$  when  $T \rightarrow T_c$ .

Then Eq. (58) becomes, using (60),

$$S_i^z = -\langle |S^z| \rangle + (1 + 2 \langle |S^z| \rangle) S_i^+ S_i^- - (1 - 2 \langle |S^z| \rangle) S_i^- S_i^+ \quad (61)$$

with the Fourier transform

$$\begin{aligned} S_q^z &= -N^{-1/2} \langle |S^z| \rangle \delta_{q,0} + N^{-1/2} (1 + 2 \langle |S^z| \rangle) \sum_q S_{q+q'}^+ S_{-q'}^- \\ &\quad - N^{-1/2} (1 - 2 \langle |S^z| \rangle) \sum_q S_{q'}^- S_{q+q'}^+. \end{aligned} \quad (62)$$

Inserting this result in the equation of motion [Eq. (8)], linearizing averaging and using Eq. (42) and (43) we obtain

$$[H, S_{q_1}^+] \approx \omega_0(q) 2 \langle |S^z| \rangle + \frac{2}{N} (2 \langle |S^z| \rangle)^2 \sum_q [J(q) - J(q_1 - q)] \gamma_2(q) \quad (63)$$

where the frequency is now

$$\omega_2(q_1) = \omega_0(q_1) 2 \langle |S^z| \rangle + (2 \langle |S^z| \rangle)^2 2N^{-1} \sum_q [J(q) - J(q_1 - q)] \varphi_2(q) \quad (64)$$

and the

$$\varphi_2(q) = \{\exp \beta[\omega_2(q)] - 1\}^{-1} \quad (65)$$

and  $\langle |S^z| \rangle$  is determined self-consistently by averaging Eq. (62). This equation has the same form as Eq. (45) for the functional relationship between  $\langle |S^z| \rangle$  and  $\Phi$ ; the frequency functions are different. The generalization of this result to arbitrary spin is to replace in the frequency  $2 \langle |S^z| \rangle$  by  $\langle |S^z| \rangle / S$  and to replace Eq. (65) by the corresponding relation for spin  $S$  found by Callen

$$\langle |S^z| \rangle = \frac{(S - \Phi)(1 + \Phi)^{2S+1} - (S + 1 + \Phi)\Phi^{2S+1}}{(1 + \Phi)^{2S+1} - \Phi^{2S+1}}. \quad (66)$$

At low temperatures the results are evaluated by expanding  $\langle |S^z| \rangle$  in  $\Phi$  which is a small quantity. The result is as we have stated

$$M(T) - M(0) = A_1 T^{3/2} + A_2 T^{5/2} + \dots + B_1 T^4 + C T^{(3/2)(2S+1)} \quad (67)$$

At high temperature ( $T \rightarrow T_c$ )

$$\Phi = \frac{1}{N} \sum_q -\frac{1}{\beta \omega^2(q)} \rightarrow \infty \quad (68)$$

and thus

$$\lim_{T \rightarrow T_c} \langle |S^z| \rangle = \frac{S(S+1)}{3} \Phi^{-1} + O(\Phi^{2-}). \quad (69)$$

The result for nearest neighbors for the Curie temperature is

$$2\beta_c J_0 = \frac{qF^2(1)}{S+1} \frac{1}{(4S+1)F(1) - (S+1)} \quad (70)$$

which for comparison with Eq. (56) for spin  $\frac{1}{2}$  is

$$\frac{1}{2} \beta_c J_0 = \frac{F^2(1)}{2F(1) - 1}. \quad (71)$$

## V. The High-Density Expansion and RPA

The RPA results are closely related to a diagram expansion which can be described as a high-density expansion in a region above  $T_c$ . After describing the basis of classification of diagrams leading to the expansion in  $1/z^*$ , with  $z^*$  the effective number of neighbors interacting with a given spin (see below), we will examine more carefully the relation between this expansion and RPA.

The analysis originally due to Brout begins with the observation that the MF is a good zero order description and that the MF Curie temperature is of the correct order of magnitude, and can be shown to be an upper limit to the true  $T_c$ . It is determined by the equation

$$2\beta_c J_0 S^2 = 1 \quad (72)$$

where

$$J_0 = \sum_j J_{ij} = \sum_v J_v z_v = J z^* \quad (73)$$

where the  $v$  enumerate shells of neighbors:

$v = 1$  nearest neighbors

$v = 2$  next nearest neighbors, etc.,

and setting  $J_1 = J$  and

$$z^* = z_1 + \sum_{j=2}^{\infty} r_j z_j \quad (74)$$

with

$$r_j = J_j/J. \quad (75)$$

Proceeding to the diagram analysis (15), we first consider for simplicity the Ising model Hamiltonian

$$H_I = - \sum_{i < j} 2J_{ij} S_i^z S_j^z + h \sum_i S_i^z. \quad (76)$$

The free energy is then

$$-\beta F = \ln \text{tr} \exp (-\beta H_I). \quad (77)$$

Separating off the single-particle term

$$-\beta F_0 = \ln \text{tr} \exp (-\beta h \sum_i S_i^z) \quad (78)$$

the contribution of the interaction is

$$-\beta F' = -\beta(F - F_0) = \ln \langle \exp (+\beta \sum_i 2J_{ij} S_i^z S_j^z) \rangle_0 \quad (79)$$

where the average  $\langle \rangle_0$  is defined

$$\langle A \rangle_0 = \text{tr } \varrho_0 A \quad (80)$$

with the weight function

$$\varrho_0 = \frac{\exp(-\beta \sum_i h S_i^z)}{\text{tr} \exp(-\beta h \sum_i S_i^z t)} = \prod_{j=1}^N \frac{\exp(-\beta h S_j^z)}{\text{tr} \exp(-\beta h S_j^z)}. \quad (81)$$

The direct expansion of the free energy is possible in terms of the quantities known as seminvariants or cumulants:  $M_n$ , which can be obtained from the generating function

$$\varphi(t) = \ln \langle e^{tx} \rangle_x = \sum_{n=1}^{\infty} \frac{t^n}{n!} M_n^{(x)} \quad (82)$$

where the symbol  $\langle \rangle_x$  indicates some defined average over the variable  $x$  and

$$M_n^{(x)} = \left( \frac{\partial^n}{\partial t^n} \varphi(t) \right)_{t=0} \quad (83)$$

with the superscript indicating the variable averaged. Thus the free energy can be expanded

$$-\beta F' = \sum_{n=1}^{\infty} \frac{\beta^n}{n!} M_n (\sum_i J_{ij} S_i^z S_j^z). \quad (84)$$

Expanding  $-\beta F'$  in diagrams for which a line bond appears for each factor  $2\beta J_{ij}$  with its endpoints (vertices) labeled  $i, j$  corresponding to the spin indices. Only linked diagrams (diagrams for which all points are connected by bonds to each other) appear in the expansion as the semi-invariant function for multiple variables in otherwise zero.

The  $n$ th order diagrams consist of the sum of all topologically distinct diagrams having  $n$  bonds the contribution to a diagram  $(n, t)$  being of  $n$ th order and of topological type enumerated by the index  $t$  consist of three factors:

- (i) A spatial factor in which a product of  $n$  factors  $2\beta J_{ij}$  with the indices corresponding to any of the possible labelings of the given topological type  $t$ . The indices are summed with no excluded volume restriction, i.e., no restriction that the different indices have no common values.
- (ii) A spin factor which is the product of a semiinvariant for each vertex,  $M_r$ , where  $r$  is the number of bonds joined to a particular vertex.
- (iii) A numerical factor  $G_{n,t}^{-1}$  where  $G_{n,t}$  is the order of the symmetry group of the diagram with all points equivalent. The extension to calculation of quantities other than the free energy is completely straightforward.

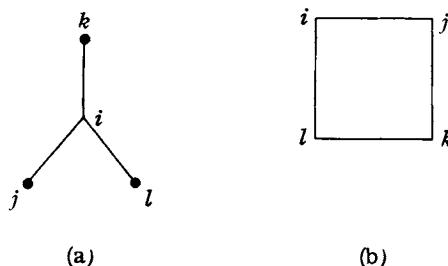


FIG. 1.

We illustrate this general result with two diagrams whose contributions are, respectively, for Fig. 1a

$$T_a = \frac{1}{3!} \sum_i \sum_j \sum_k \sum_l (2\beta)^3 J_{ij} J_{ik} J_{il} M_3^{(i)} M_1^{(j)} M_1^{(k)} M_1^{(l)} \quad (85)$$

and for Fig. 1b

$$T_b = \frac{1}{2} \frac{1}{4} \sum_{ijkl} (2\beta)^4 J_{ij} J_{jk} J_{kl} J_{li} (M_2)^4 \quad (86)$$

where we have here dropped the superscript indicating the spin averaged the result being independent of that for the homogeneous system assumed. For example for spin  $\frac{1}{2}$  the semiinvariants appearing here are

$$M_1 = \langle S^z \rangle = \frac{1}{2} \tanh \beta h \frac{1}{2} \quad (87)$$

$$M_2 = \langle S^z \rangle - \langle S^z \rangle^2 = \frac{\partial}{\partial \beta h} M_1 = \frac{1}{4} \operatorname{sech}^2 \frac{1}{2} \beta h \quad (88)$$

$$\begin{aligned} M_3 &= \langle (S^z)^3 \rangle - 3 \langle (S^z)^2 \rangle \langle S^z \rangle + 2 \langle S^z \rangle^3 = \frac{\partial^2}{\partial \beta h^2} M_1 \\ &= -\frac{1}{4} \tanh \beta h \frac{1}{2} \operatorname{sech}^2 \frac{1}{2} \beta h . \end{aligned} \quad (89)$$

Performing the sums over indices in Eq. (85) we obtain

$$T_a = N/3! (2\beta J_0 M_1)^3 M_3 \quad (90)$$

and introducing the Fourier transform of  $J_{ij}$ ,  $J(q)$  Eq. (86) becomes

$$T_b = \frac{1}{2} \frac{1}{4} \sum_q (2\beta J(q) M_2)^4 . \quad (91)$$

Let us now disregard the spin factors or replace them by a suitable average. For  $T \gtrsim T_c$ ,  $\beta/\beta_c \approx 1$ ; thus each bond contributes

$$2\beta J \approx 2\beta_c J(\beta/\beta_c) \approx 1/z^* \quad (92)$$

in view of Eq. (72). In diagrams of order  $n$  with no closed paths such as Fig. 1a, each diagram has  $n+1$  vertices and  $n$  bonds. One vertex contributes  $N$  and each of the others gives a factor  $z^*$  hence the net contribution is

$$(z^*)^n \times 1/z^* = 1$$

and the diagrams are independent of  $z^*$ . A summation of all such diagrams (Cayley trees) yields MF. If we introduce one closed path in a diagram we lose a free summation on an index and hence we lose a factor of  $z^*$ ; hence such diagrams are of order  $1/z^*$ , etc.

The term  $T_a$  is a prototype of the  $(1/z^*)^0$  series and the term  $T_b$  of the  $1/z^*$  series. The latter gives the series

$$\frac{1}{2} \sum_{n=1}^{\infty} \sum_q \frac{[2\beta J(q) M_2]^n}{n} = -\frac{1}{2} \sum_q \ln [1 - 2\beta J(q) M_2] \quad (93)$$

where we have used  $\sum J(q) = 0$  to add the  $n=1$  term.

The corresponding energy is

$$E^{(1)} = \frac{1}{2} \sum \frac{2J(q)M_2}{1 - 2\beta J(q)M_2} . \quad (94)$$

The effect of the addition of tree diagrams attached to the diagrams of the series (93) is still of order  $1/z^*$ ; the resulting sum is of the same

form as above except that the semiinvariants are replaced by the identical function of the effective field  $h + 2\beta J_0$  instead of the external field  $h$ .

An expansion analogous to that described following Eq. (84) can be obtained for the Heisenberg Hamiltonian (16). The difference lies in the necessity that for a generalization of the semiinvariants due to the noncommutativity of the spin operators. As our interest is in the  $1/z^*$  classification and we are merely quoting results we will refrain from explicitly introducing here the form of the generalization. Suffice it to say that in the resulting expansion the spatial factor is the same as described above and the spin factor is again a product of the (generalized) semiinvariants for each spin index. Again considering some kind of average for the spin factors, the criterion of classification remains the same as in the Ising problem. Zeroth order comprises diagrams having no closed paths and in fact involves only  $S^z$  operators as  $\langle S^\pm \rangle = 0$ ; thus; this again leads to MF. First order in  $1/z^*$  comprises diagrams having a single closed loop, the previously demonstrated longitudinal terms in addition to diagrams with a single transverse loop. At low temperatures to order  $1/z^*$  we obtain spin wave results up to terms exponential in  $-2\beta J$ . The RPA result thus appears as a rather attractive interpolation between a low-temperature series and an expansion in  $1/z^*$  at high temperatures. Above  $T_c$  for vanishing external field the contribution of transverse rings is equal to just twice that of longitudinal. In order not to get grossly inconsistent results for the phase transition a modification of this expansion was found necessary. In the form obtained this modified  $1/z^*$  expansion is closely related to the spherical model above the Curie temperature which is identical with the RPA result for  $T > T_c$ . When we evaluate the modified  $1/z^*$  diagrams for low temperatures we obtain the spurious  $T^3$  result and generally similar to the low-temperature behavior of RPA. To describe diagrammatically the modified  $1/z^*$  expansion, we consider a class of reducible diagrams having articulation points; i.e., points at which the diagram can be cut into two or more disjoint pieces. Then instead of including only tree diagrams and diagrams with a single loop we consider all diagrams which when cut at all articulation points comprise either loops or a single bonds. The result of summing this class of diagrams is a renormalized  $1/z^*$  criterion and a result closely analogous to the spherical model

above  $T_c$ . Brout (3a) by an almost equivalent renormalization finds exactly the spherical model results above  $T_c$ . Thus the RPA results above  $T_c$  are equivalent to the high density approximation in the form we have described.

These results have however a rather serious difficulty in their behavior near  $T_c$ . The origin of the difficulty can most easily be seen in the diagram analysis. Differentiating the free energy twice to obtain the susceptibility, for example, is equivalent to introducing graphs which are omitted in the partial diagram summation. One violates an identity similar to a Ward identity, a relationship between a vertex and bond renormalization. In particular here the functions introduced in this way are singular at  $T_c$  and thus strongly effect the results; i.e., effectively with the form of renormalization used, the  $1/z^*$  expansion evidently breaks down as  $T \rightarrow T_c$ . For the Ising model this problem has been examined by Englert (17) who also summed all convolution diagrams. He suggests that this might be a more adequate high-density form, but this is yet to be shown; the Ward identity violation remains. At low temperatures the spurious  $T^3$  effects can be accounted for, but the difficulties with the transition region result not only in the judgment that these approximations are too crude to treat the very sensitive behavior of a phase transition, but they also raise the question as to the meaningfulness of the expansion parameter. The resolution of this question is yet to be found.

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# **Renormalization in Equilibrium Statistical Mechanics**

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## **I. Introduction**

We are concerned with “renormalization” equilibrium statistical mechanics. By renormalization we mean that we wish to express the thermodynamical functions describing a system not in terms of the (“bare”) potentials occurring in the Hamiltonian but in terms of observable quantities (or quantities directly related to observables) like the distribution functions. We shall consider successively normal systems and “superfluid” systems; we shall review the present status of the renormalization program and discuss in general terms the salient features of the existing renormalized formulations. As for Section IV of these notes, which should have contained the explicit construction of renormalized formulations of statistical mechanics, the reader is referred to material already published (1–3).

## **II. Normal Systems**

### **A. EXPRESSION IN TERMS OF POTENTIALS**

Consider a normal system (superfluid systems are considered later) described by the Hamiltonian

$$H = \sum \nu_1(x_1, x_1') a_{x_1}^+ a_{x_1'} + \sum \nu_2(x_1, x_2; x_1', x_2') a_{x_1}^+ a_{x_2}^+ a_{x_1'} a_{x_2'}.$$

Here  $\nu_1$  describes the one-body part of the Hamiltonian (i.e., the kinetic energy minus the chemical potential  $\mu$  and possibly a one-body external

potential),  $\nu_2$  is the usual two-body interaction potential. For simplicity, we consider only one type of particles fermions or bosons;  $a_x^+$  is the operator creating one such particle in a state  $x$  [ $x$  momentum (or position) and spin].

The grand partition function describing the system is defined by

$$Z = \exp(W) = \text{trace } \exp(-\beta H) \quad (1)$$

where  $\beta = (\text{Boltzmann constant} \times \text{temperature})^{-1}$ . This definition expresses  $W$  as a functional of the potentials let  $W[\nu_1, \nu_2]$ . An explicit form of  $W[\nu_1, \nu_2]$  which is sometimes easier to manipulate than the compact form [Eq. (1)] is furnished by perturbation expansions.

The one- and two-particle distribution functions are defined by

$$G_1(x_1, x_1') = - \frac{\delta}{\delta \beta \nu_1(x_1, x_1')} W[\nu_1, \nu_2] \quad (2)$$

$$G_2(x_1, x_2; x_1', x_2') = - \frac{\delta}{\delta \beta \nu_2(x_1, x_2; x_1', x_2')} W[\nu_1, \nu_2]. \quad (3)$$

## B. MASS RENORMALIZATION

Instead of  $W$ , consider now the “free energy”

$$F^{(1)} = W[\nu_1, \nu_2] + \beta \int \nu_1(x_1, x_1') G_1(x_1, x_1') dx_1, dx_1'. \quad (4)$$

Through Eq. (2)  $\nu_1$  may be considered as implicitly given in terms of  $G_1$  (and  $\nu_2$ ) and through Eqs. (2) and (4)  $F^{(1)}$  is given as a functional of  $G_1$  and  $\nu_2$ , which verifies the relation

$$\beta \nu_1(x_1, x_1') = \frac{\delta}{\delta G_1(x_1, x_1')} F^{(1)}[G_1, \nu_2]. \quad (5)$$

This relation inverts Eq. (2) and carries out “mass” renormalization since the “bare” potential  $\nu_1$  being expressed in terms of its conjugate variable, the one-particle distribution function  $G_1$ . The problem is reduced to constructing explicitly the right-hand side of Eq. (5).

## C. VARIATIONAL PROPERTIES

The properties of the system after mass renormalization are conveniently described by considering the functional

$$\hat{W} = F(\hat{G}_1, \nu_2) - \beta \int v_1(x_1, x_1') \hat{G}_1(x_1, x_1') dx_1 dx_1' \quad (6)$$

where  $v_1$  has a fixed value. Under variations of  $\hat{G}_1$ ,  $\hat{W}$  remains stationary when Eq. (2) is verified, i.e., when the variations are made around the values  $\hat{G}_1 = G_1$  and

$$\hat{W} = W = F(G_1, \nu_2) - \beta \int v_1(x_1, x_1') G_1(x_1, x_1') dx_1 dx_1'. \quad (7)$$

Besides, around these values the second variation is given by

$$\int \delta \hat{G}_1(x_1, x_1') \delta \hat{G}_1(x_2, x_2') \frac{\delta^2}{\delta G_1(x_1, x_1') \delta G_1(x_2, x_2')} F(G_1, \nu_2)$$

where

$$\frac{\delta^2}{\delta G_1(x_1, x_1') \delta G_1(x_2, x_2')} F[G_1, \nu_2] = \beta \frac{\delta \nu_1}{\delta G_1(x_2, x_2')} [x_1, x_1'; G_1] \quad (8)$$

where Eq. (5) has been used to write Eq. (8). Now, considered as a matrix in  $x_1, x_1'$ , and  $x_2, x_2'$  the right-hand side of (8) is the inverse matrix of

$$\frac{\delta G_1}{\delta \beta \nu_1(x_2, x_2')} [x_1, x_1'; \nu_1] = - \frac{\delta^2}{\delta \beta \nu_1(x_1, x_1') \delta \beta \nu_1(x_2, x_2')} W[\nu_1, \nu_2]$$

which has the structure of a fluctuation and is immediately displayed as a negative definite matrix. The second variation is thus always negative and for  $\hat{G}_1 = G_1$ , the functional reaches its absolute maximum  $\hat{W} = W$ .

It is interesting to notice that the Jacobian of the transformation  $\nu_1 \leftrightarrow G_1$  is given by the right-hand side of Eq. (8), and its zeroes correspond to infinite fluctuations, and possible vanishing of the second variation. A simple example of this phenomenon occurs in homogeneous classical systems, where the vanishing of the second variation signals that system has become unstable.

## D. DISCUSSION

This ideal program of mass renormalization is reduced to constructing explicitly the right-hand side of Eq. (5), e.g., as an expansion in powers of  $G_1$  and  $\nu_2$ . In this sense this program has been achieved long ago for classical systems by Yvon (4) who repeatedly emphasized the importance of renormalization in connection with phase transition problems. Substitution of  $\nu_1$  as given by Eq. (5) into Eq. (7) leads to the classical virial expansion (in terms of the one-particle distribution function).

For quantum systems the corresponding results are yet unknown. Several formulations have gone some way in that direction in the sense that they partially eliminate  $\nu_1$ , i.e., the right-hand side of Eq. (5) is expressed in terms of  $G_1$  (and  $\nu_2$ ) but some residual dependence upon  $\nu_1$  is left over.

(a) Lee and Yang (5) have expressed  $\nu_1$  in terms of  $e^{\beta u} G_1$ ,  $\nu_2$  and some residual dependence upon  $\nu_1$ . They were the first to exhibit the stationarity and (for Bose systems) the maximum property.

(b) A different formulation (6) which gives back term by term the virial expansions in the classical limit, expresses  $\nu_1$  in terms of  $G_1$ ,  $\nu_2$ , and a residual dependence upon  $\nu_1$ . The functional appearing in this formulation has an absolute maximum at its stationarity point for all systems. The residual dependence upon  $\nu_1$  in the functional  $\hat{W}$  is due to the fact that, in this case, one actually considers

$$\exp(\hat{W}) = \text{trace } \exp(-\beta H) \exp(-\beta \hat{H}_1) \quad (9)$$

$$\hat{H}_1 = \sum \hat{\nu}_1(x_1, x_1') a_{x_1}^+ a_{x_1}^-.$$

with

$$\hat{G}_1(x_1, x_1') = - \frac{\delta W}{\delta \beta \hat{\nu}_1(x_1, x_1')} [\nu_1, \nu_2; \nu_1]. \quad (10)$$

After elimination of  $\hat{\nu}_1$  (but not of the  $\nu_1$  appearing in  $H$ ) one obtains a  $\hat{W}$

$$\hat{W} = F(\nu_1, \nu_2; \hat{G}_1) + \beta \int \hat{\nu}_1(x_1, x_1'; \hat{G}_1(x_1, x_1'))$$

which has the properties described above.

(c) Formally very similar to the “classical-like” formulation (b), a “Landau-like” formulation (7) is also possible which expresses  $\nu_1$  in

terms of a  $\Gamma_1$  (distribution function for "quasi particles"),  $\nu_2$ , and a residual dependence upon  $\nu_1$ . In the zero temperature limit this formulation yields the results of Landau (8) for Fermi liquids.

(d) It is possible, however, to fulfill the renormalization program if one allows for the introduction of "time" dependent (a "time" varying between 0 and  $\beta$ )  $\nu_1$  potentials and conjugate distribution functions. The "time" dependent  $\nu_1$  potentials serve the purpose of generating the conjugate "time" dependent distribution function which for usual systems appears as one-body Green's function

$$G_1(x_1 u_1, x_1' u_1') = \frac{\text{trace } T [\exp(-\beta H) a_{x_1}^+(u_1) a_{x_1'}(u_1')]}{\text{trace } \exp(-\beta H)} \quad (11)$$

$$0 < u_1, u_1' < \beta$$

where  $T$  stands for the  $T$  product operator. In that formulation the Dyson equation (9, 10),

$$[G_1^0]^{-1}(x_1, u_1; x_1', u_1') = [G_1]^{-1}(x_1, u_1; x_1', u_1') \quad (12)$$

$$+ K_1 \{x_1, u_1; x_1', u_1'; G_1, \nu_2\}$$

where  $-K_1$  is the usual mass operator and  $G_1^0$  the one-body Green's function for the system without the interaction  $\nu_2$ , furnishes the equivalent of Eq. (5), thus expressing  $\nu_1$  in terms of the time-dependent one-body distribution function. More explicitly Eq. (12) writes

$$\frac{\delta F^{(1)}[G_1, \nu_2]}{\delta G_1(x_1, u_1; x_1', u_1')} = -\delta(u_1 - u_1') \delta(x_1 - x_1') \frac{\partial}{\partial u_1} \quad (13)$$

$$+ [G_1]^{-1}(x_1, u_1; x_1', u_1') + K_1 \{x_1, u_1; x_1', u_1'; G_1, \nu_2\}$$

leading immediately (10) to  $F^{(1)}[G_1, \nu_2]$  by functional integration. Here the mass renormalization has thus been performed by paying the price of introducing a time-dependent distribution function which leads to no definite sign for the second functional derivative

$$\frac{\delta^2}{\delta G_1(x_1 u_1, x_1' u_1') \delta G_1(x_2 u_2, x_2' u_2')} F^{(1)}[G_1, \nu_2].$$

## E. VERTEX RENORMALIZATION

Instead of  $F^{(1)}$ , consider now the entropy

$$\begin{aligned} F^{(2)} = & W[\nu_1, \nu_2] + \beta \int [\nu_1(x_1 x_1') G_1(x_1 x_1') dx_1 dx_1' \\ & + \nu_2(x_1 x_2, x_1' x_2') G_2(x_1 x_2, x_1' x_2') dx_1 dx_2 dx_1' dx_2'] \end{aligned} \quad (14)$$

which considered through Eqs. (2) and (3) as a functional of  $G_1, G_2$  verifies the relations ( $j = 1, 2$ )

$$\beta \nu_j = \frac{\delta}{\delta G_j} F^{(2)}[G_1, G_2]. \quad (15)$$

Relations (15) invert Eqs. (2) and (3) and fulfill the renormalization program for systems involving only one- and two-body potentials, since Eq. (15) expresses the “bare” potentials  $\nu_1, \nu_2$  in terms of the distribution functions  $G_1, G_2$ . Again the functional

$$\begin{aligned} \hat{W} = & F^{(2)}[\hat{G}_1, \hat{G}_2] - \beta \int [\nu_1(x_1 x_1') \hat{G}_1(x_1 x_1') dx_1 dx_1' \\ & + \nu_2(x_1 x_2, x_1' x_2') \hat{G}_2(x_1 x_2, x_1' x_2') dx_1 dx_2 dx_1' dx_2'] \end{aligned} \quad (16)$$

remains stationary when variations  $\delta \hat{G}_1, \delta \hat{G}_2$  are made around the value  $\hat{G}_1 = G_1, \hat{G}_2 = G_2$  and at that point  $\hat{W}$  is equal to  $W$  and is an absolute maximum.

Notice that the stationarity condition upon  $\hat{W}$  is identical to a stationarity condition upon  $F^{(2)}[\hat{G}_1, \hat{G}_2]$  under the constraint that the average energy

$$\begin{aligned} E = & \int [\nu_1(x_1 x_1') \hat{G}_1(x_1 x_1') dx_1 dx_1' \\ & + \nu_2(x_1 x_2, x_1' x_2') \hat{G}_2(x_1 x_2, x_1' x_2') dx_1 dx_2 dx_1' dx_2'] \end{aligned}$$

is being kept constant;  $\beta$  appears thus, in Eq. (16), as a Lagrange multiplier.

As far as results are concerned, the full renormalization scheme is on par with the mere mass renormalization. The right-hand side of Eq. (15) is only explicitly known for classical systems (12, 13). For quantum systems, only partial eliminations of  $\nu_1$  and  $\nu_2$  have been so far performed

(for example, it has been carried out in the Lee-Yang formulation (15) where some residual dependence upon  $\nu_1$  and  $\nu_2$  is left over).

Again if one is willing to introduce time-dependent distribution functions (11) and

$$G_2(x_1 u_1, x_2 u_2; x_1' u_1', x_2' u_2') = \frac{\text{trace } T \exp(-\beta H) a_{x_1}^+(u_1) a_{x_2}^+(u_2) a_{x_1'}(u_1') a_{x_2'}(u_2')}{\text{trace } \exp(-\beta H)}. \quad (17)$$

the equivalent of Eq. (15) and of the entropy  $F^{(2)}$  can be written explicitly (13) in terms of  $G_1(x_1 u_1, x_1' u_1')$  and  $G_2(x_1 u_1, x_2 u_2; x_1' u_1', x_2' u_2')$  and the renormalization performed; but the definiteness in sign of the second functional derivative is lost.

#### F. DEPENDENCE UPON THE EQUILIBRIUM PARAMETER

The equilibrium parameters  $\beta$  and  $\beta\mu$  only occur in the combinations  $\beta\nu_1$  and  $\beta\nu_2$ . In the complete elimination of  $\nu_1$  and  $\nu_2$ , the equilibrium parameters disappear and the entropy  $F^{(2)}[G_1, G_2]$  in its explicit form no longer contains  $\beta$ ,  $\beta\mu$  (nor  $\nu_1$  or  $\nu_2$ ). The functional  $F^{(2)}[\hat{G}_1, \hat{G}_2]$  is thus only dependent upon the fact that the original Hamiltonian contains two-body forces (no  $n$ -body forces,  $n \geq 3$ ); it preserves no memory of the dynamics of the system nor of its equilibrium parameters. Whether the functional  $F^{(2)}$  may be given a meaning for systems perturbed out of their equilibrium, in the sense that the Boltzmann  $H$ -function does for an approximate form of the entropy, is not known.

It is interesting to note that in the "Landau-like" formulation, quoted in Section II, D (c), the equilibrium parameters also disappear. Namely, in this case, the entropy functional is formally identical with that of a noninteracting system, i.e., for a Fermi system

$$F^{(2)} = -\text{trace } \{(1 - \hat{I}) \log(1 - \hat{I}) + \hat{I} \log \hat{I}\}. \quad (18)$$

The system at equilibrium is then described by looking for stationary solutions of  $F^{(2)}$  under the constraint of constant average energy, where the average energy is expressed as

$$E = E\{\hat{I}; \nu_1, \nu_2\}. \quad (19)$$

$E\{\hat{F}; \nu_1, \nu_2\}$  is a functional of  $\hat{F}$  given by an infinite series expansion in  $\nu_1, \nu_2, \hat{F}$  where  $\beta$  (and  $\beta\mu$ ) do not appear. At the stationarity point, e.g., in momentum representation,  $\hat{F}(k) = \Gamma(k)$  which may be called the average occupation number for quasi particles.

In all other formulations quoted above  $F^{(2)}$  was an infinite expansion in powers of  $G_1, G_2$ , the constraint itself being linear in those variables. Here  $F^{(2)}$  has an extremely simple form but the constraint equation contains an infinite expansion in  $\nu_1, \nu_2, \hat{F}$ .

### G. WHY RENORMALIZATION?

One may ask why it is desirable to carry out the renormalization procedure. Clearly to obtain the thermodynamical functions in terms of observable quantities is certainly a desirable feature in itself.

For an actual calculation one is reduced to take approximate forms of the thermodynamical functions. In perturbation theory, for example, one would truncate  $W[\nu_1, \nu_2]$  to a given order in  $\nu_1, \nu_2$ . In the mass renormalized form, keeping  $F^{(1)}[G_1, \nu_2]$  [and correspondingly  $\delta F^{(1)}/\delta G_1$  in Eq. (5)] up to first order in  $\nu_2$  generates the (self-consistent) Hartree-Fock approximation; to obtain the same result in the perturbation expansion would have necessitated the re-summation of an infinite series of terms. Likewise truncation of the functional  $F^{(2)}$  [and of Eq. (15) correspondingly] will generate “doubly” self-consistent equations, obviously harder to solve, which embed infinite re-summations of terms of  $W$  or  $F^{(1)}$  and are presumed to have better convergence properties, and to be better adapted to the description of phase transitions.

However, approximations generated in the above-described way are not necessarily the best for all purposes. These approximations respect the relation implied by the pair of equations (15) but they always violate the relation

$$\frac{\delta^2}{\delta \beta \nu_1(x_1 x_1') \delta \beta \nu_1(x_2 x_2')} W[\nu_1, \nu_2] = G_2(x_1 x_2, x_1' x_2') - G_1(x_1 x_1') G_1(x_2 x_2') \quad (20)$$

implied by the Hamiltonian structure. Relation (20) is a functional relation between  $G_1$  and  $G_2$

$$-\frac{\delta}{\delta \beta \nu_1(x_2 x_2')} G_1(x_1 x_1') = G_2(x_1 x_2, x_1' x_2') - G_1(x_1 x_1') G_1(x_2 x_2') \quad (21)$$

which is related to current conservation. On the other hand, there are cases where it is important (to study collective excitations like sound waves, for example) to embed in the approximations chosen the consequences of current conservation (14); in such a case, one would not truncate  $F^{(2)}$  but rather  $F^{(1)}$  and relation (21) would be used to define  $G_2$ .

Finally, there are systems where the renormalization procedure becomes a necessity. This is the case of systems where one cannot afford to use expansions in some of the potentials occurring in the Hamiltonian. Systems with hard core interactions are one example. A second example is furnished by superfluid systems.

### III. Superfluid Systems

#### A. EXTENDED ENSEMBLE

The treatment of superfluid systems (like Bose systems at low temperature) by the methods described above lead to serious convergence difficulties. These difficulties are due to the Bose condensation phenomenon, i.e., the macroscopic occupation of an individual state. Extensions of the grand canonical ensemble have been introduced to describe such systems and avoid convergence difficulties.

Lee and Yang (15) have proposed an extended ensemble where the density matrix

$$\varrho = \exp(-\beta H) / \text{trace } \exp(-\beta H)$$

is replaced (in order to describe a possible condensation in the state of momentum  $k = 0$ ) by

$$\varrho_y = \exp(-y) \frac{y^{n_0}}{n_0!} \exp(-\beta H) / \text{trace } \exp(-y) \frac{y^{n_0}}{n_0!} \exp(-\beta H).$$

$n_0$  is the occupation number operator for the state  $k = 0$  ( $n_0 = a_0^+ a_0$ ).  $y$  is a free parameter ( $y$  stands here for the  $x$  used by Lee and Yang times the volume) determined by the condition that  $W_y$  defined by

$$W_y = \text{trace } \exp(-y) \frac{y^{n_0}}{n_0!} \exp(-\beta H) \quad (23)$$

is stationary under variation of the number  $y$ . At the stationary point  $\bar{y}$  (and for infinite systems),  $W_{\bar{y}}$  is shown to be equal to the usual  $W$  and  $\bar{y}$  to be the true macroscopic occupation number of the state  $k = 0$ .

Bogoliubov (16) has suggested the introduction of a different ensemble which is for our purposes more convenient to describe superfluid systems or more generally systems which are degenerate in their statistical equilibrium. To describe systems where condensation is supposed to occur in the state of momentum  $k = 0$ , the Hamiltonian of the system is supplemented by an (infinitesimal) "source" term

$$H_s = \nu_{1/2} a_0^+ + \nu_{1/2}^* a_0$$

where  $\nu_{1/2}$  is the source potential ( $\frac{1}{2}$ -body potential; in this case,  $\nu_{1/2}$  is reduced to a constant). P. C. Martin (1) has discussed and emphasized the usefulness of introducing a generalized source term

$$H_s = \int [\nu_{1/2}(x) a_x^+ + \nu_{1/2}^*(x) a_x] dx \quad (24)$$

which serves the purpose of generating equations of motion of a more complex structure describing situations where the translational invariance is violated (vortex lines).

More precisely consider now

$$\exp(W_s) = \text{trace } \exp[-\beta(H + H_s)] \quad (25)$$

$W_s$  being thus a functional  $W_s[\nu_{1/2}, \nu_{1/2}^*, \nu_1, \nu_2]$ . The conjugate variables associated with the source potentials  $\nu_{1/2}, \nu_{1/2}^*$  are

$$G_{1/2}(x) = -\frac{\delta}{\delta \beta \nu_{1/2}^*(x)} W[\nu_{1/2}, \nu_{1/2}^*, \nu_1, \nu_2] \quad (26)$$

(and its complex conjugate).  $G_{1/2}^*(x)$  plays the role of a renormalized wave function for the condensate. We may now consider

$$\begin{aligned} F^{(1/2)} = & W_s[\nu_{1/2}, \nu_{1/2}^*, \nu_1, \nu_2] + \beta \int [\nu_{1/2}(x) G_{1/2}^*(x) \\ & + \nu_{1/2}^*(x) G_{1/2}(x)] dx \end{aligned} \quad (27)$$

as a functional of  $G_{1/2}$ ,  $G_{1/2}^*$  (and  $\nu_1$ ,  $\nu_2$ ) through Eq. (26). We have again

$$\nu_{1/2}^*(x) = \frac{\delta}{\delta G_{1/2}(x)} F^{(1/2)}[G_{1/2}, G_{1/2}^*, \nu_1, \nu_2]. \quad (28)$$

This equation inverts Eq. (26). The functional

$$\hat{W}_s = F^{(1/2)}[\hat{G}_{1/2}, \hat{G}_{1/2}^*, \nu_1, \nu_2] - \beta \int [\nu_{1/2}(x) G_{1/2}^*(x) + \nu_{1/2}^*(x) G_{1/2}(x)] dx \quad (29)$$

where  $\nu_{1/2}$  and  $\nu_{1/2}^*$  are kept fixed, is stationary and maximum for variations  $\delta\hat{G}_{1/2}$ ,  $\delta\hat{G}_{1/2}^*$  around  $\hat{G}_{1/2} = G_{1/2}$ ,  $\hat{G}_{1/2}^* = G_{1/2}^*$ .

In the limit of a vanishingly small source term the system is described by the functional

$$W_s \rightarrow F^{(1/2)}[G_{1/2}, G_{1/2}^*, \nu_1, \nu_2], \quad (30)$$

supplemented by the stationarity equation

$$\frac{\delta F^{(1/2)}}{\delta G_{1/2}(x)} = 0 \quad (31)$$

and a positive definiteness condition. Above the transition temperature Eq. (31) admits only the trivial solution  $G_{1/2} = 0$  and  $F^{(1/2)}$  reduces to  $W[\nu_1, \nu_2]$ . The same procedure is extended with no difficulty to superfluid Fermi systems.

Clearly the renormalization procedure is here essential, since the bare potential  $\nu_{1/2}$  is allowed to vanish, whereas it is assumed that domains exist where the conjugate (renormalized) quantity  $G_{1/2}^*$  is non-vanishing.

## B. RENORMALIZATION

Consider the one-body distribution function in the ensemble with source (eventually the source is always supposed to vanish)

$$\begin{aligned} G_1(x_1, x_1') &= -\frac{\delta}{\delta \beta \nu_1(x_1 x_1')} W_s \\ &= \text{trace exp}[-\beta(H + H_s)] a_{x_1}^+ a_{x_1'} / \text{trace exp}[-\beta(H + H_s)] \\ &= \langle a_{x_1}^+ a_{x_1'} \rangle. \end{aligned}$$

It can now be rewritten as

$$\begin{aligned} G_1(x_1 x_1') &= \langle a_{x_1}^+ \rangle \langle a_{x_1'} \rangle + \langle (a_{x_1}^+ - \langle a_{x_1}^+ \rangle) (a_{x_1'} - \langle a_{x_1'} \rangle) \rangle \\ &= G_{1/2}^*(x_1) G_{1/2}(x_1') + \tilde{G}_1(x_1, x_1'). \end{aligned} \quad (32)$$

$\tilde{G}_1$  is the cumulant part of  $G_1$  and this splitting of one-body distribution function for superfluid system in configuration space, corresponds to the one first introduced by Penrose and Onsager (17); here  $\tilde{G}_1$  tends to zero as  $(x_1 - x_1') \rightarrow \infty$ . The total number of particles of the system is given by

$$\int G_1(x_1, x_1) dx_1 = \int |G_{1/2}(x_1)|^2 dx_1 + \int \tilde{G}_1(x_1, x_1) dx_1, \quad (33)$$

the first term being the condensate contribution.

Quantities like  $\langle a_{x_1}^+ a_{x_1'}^+ \rangle$ ,  $\langle a_{x_1} a_{x_1'} \rangle$  are now generally nonvanishing and the matrix notation introduced by Nambu (18) becomes very useful. One works with a one-body distribution function which (besides being a matrix in  $x_1, x_1'$ ) is now a  $2 \times 2$  matrix  $\mathbf{G}_1(x_1, x_1')$  the elements of which are  $\langle a_{x_1}^+ a_{x_1} \rangle$ ,  $\langle a_{x_1} a_{x_1'}^+ \rangle$ ,  $\langle a_{x_1}^+ a_{x_1'}^+ \rangle$  and  $\langle a_{x_1} a_{x_1'} \rangle$ . The mass renormalization is then carried out in the same way as was done for normal systems. The explicit knowledge of the renormalized functional has reached about the same stage as for normal systems.

(a). Lee and Yang (15) have obtained (in their extended ensemble) a  $W$  functional of  $y$  and  $e^{\beta\mu}\tilde{\mathbf{G}}_1$ , which, for the Bose systems considered, is stationary and maximum under variations of  $y$  and  $e^{\beta\mu}\tilde{\mathbf{G}}_1$ .

(b, c). The “classical-like” and the “Landau-like” formulations can also be extended to superfluid systems. The former, besides being actually stationary and maximum under variations of  $\mathbf{G}_{1/2}$  and  $\mathbf{G}_1$ , presumably has only an academic interest. The latter leads to a microscopic formulation of the Landau theory of the Bose liquid (or superfluid Fermi liquids) (6).

(d). All these formulations, as was described in Section II, D, do not eliminate completely the one-body potential  $v_1$ ; but this elimination is possible if one again introduces time-dependent one-body distribution functions  $\mathbf{G}_1(x_1 u_1, x_1' u_1')$ . Indeed, as for normal systems the full renormalization program (eliminating completely  $v_{1/2}, v_1, v_2$ ) has been carried

out explicitly for the time-dependent formulation and only for that formulation (1, 2, 3).

The entropy  $F^{(2)}$  has been exhibited as a functional of  $\tilde{\mathbf{G}}_1$ ,  $\tilde{\mathbf{G}}_{3/2}$ ,  $\tilde{\mathbf{G}}_2$ , respectively, the cumulant parts of the time-dependent matrices built with two, three, and four operators  $a_x(u)$  or  $a_x^+(u)$  (i.e.,  $2^j$  matrices  $j = 2, 3, 4$ ).  $F^{(2)}$  turns out to be independent of  $\mathbf{G}_{1/2}$ . Besides, the remarks made in Section II, F are also valid for superfluid systems.

#### IV. Explicit Construction of the Functionals

We have so far completed in general terms a review of the present status of "renormalized" equilibrium statistical mechanics. Explicit construction techniques of the functionals described in Sections II and III will not be reproduced here as they are already in the published literature. For the source ensemble treatment of superfluid systems the reader is referred to refs. (1, 2, 3) where algebraic and diagrammatic techniques respectively, are described.

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# **Liouville Representation of Quantum Mechanics with Application to Relaxation Processes**

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## **I. Introduction**

It has been pointed out in the past (*1*) that the representation of quantum mechanical states by means of a density matrix has the following features: (a) each element  $\varrho_{mn}$  of this matrix represents the mean value of an observable physical quantity; (b) the whole square array of elements  $\varrho_{mn}$  may be regarded as the set of components of a vector in an appropriate space and may be replaced by a set of real components; (c) the Schrödinger-von Neumann equation which governs the time dependence of  $\varrho$  represents a rotation of this vector; (d) the answer to physical questions of interest pertaining to a large physical system is represented by the projection of the vector on a very small subspace and by the time variations of this projection.

These circumstances enable one to formulate many-body problems in a manner that is compact, adherent to physical observations, and closely related to the corresponding classical treatment. The potentialities of this method have been exploited by Zwanzig (*2-4*) and developed further in a recent paper (*5*) which deals specifically with the shift and broadening of spectral lines of a gas due to the interaction among gas molecules.

These lectures have the following aims: (1) to give a self-contained presentation of the vector space formalism which is called the Liouville representation of quantum mechanics, and (2) to apply this formalism to a “system” of interest, which possesses a rather small number of degrees of freedom but interacts with a “bath,” i.e., with a much larger system whose role is merely to act as a noisy disturbance or a thermal

reservoir. Most of the material to be presented is included in ref. (5) but these lectures lay greater emphasis on its general aspects. Green's function methods and other modern techniques for the treatment of many-body problems may be regarded as special cases, or forms, of the Liouville representation, somewhat as wave mechanics is a special case of Dirac's transformation theory. Thus the Liouville representation emphasizes aspects that are common to a large variety of phenomena.

## II. The Liouville Representation

### A. THE DENSITY MATRIX

We call "state" of a physical system the information about the system which is required, in addition to knowledge of its fixed properties and of physical laws, to predict the outcome of any experiment performed on it. In quantum mechanics such predictions take the form of ensemble mean values of Hermitian operators,  $\langle A \rangle$ ,  $\langle B \rangle$ , .... (Notice that the probability of success of a "yes-no" experiment may be regarded as the mean value of an operator with eigenvalues 1 and 0.) Thus we can describe the state of a system by whatever set of parameters suffices, in addition to standard data, to predict the mean value of its Hermitian operators.

To this end we take advantage of the linearity of the averaging process, which is represented by the equation  $\langle \alpha A + \beta B \rangle = \alpha \langle A \rangle + \beta \langle B \rangle$ , where  $\alpha$  and  $\beta$  are arbitrary numbers. The mean value of an operator  $A$  with the matrix representation  $A_{mn}$  can then be expressed in the form

$$\langle A \rangle = \sum_{mn} A_{mn} \langle U^{(mn)} \rangle, \quad (1)$$

where  $U^{(mn)}$  is an operator whose matrix has the element  $(m, n)$  equal to 1 and all others equal to 0. This operator is expressed in terms of (pure) state representatives  $u_m$ , belonging to a complete orthonormalized set of states, and of their conjugates  $u_m^\dagger$  or in terms of the corresponding Dirac symbols  $| m \rangle$ ,  $\langle m |$ , by

$$U^{(mn)} = u_m u_n^\dagger = | m \rangle \langle n |. \quad (2)$$

Knowledge of  $\langle U^{(mn)} \rangle$  for all ordered pairs  $(m, n)$  describes the state of the system, because Eq. (1) applies to an arbitrary  $A$ .

Since, according to Eq. (2),  $U^{(nm)} = U^{(mn)\dagger}$ , the set of mean value  $\langle U^{(mn)} \rangle = \langle U^{(nm)} \rangle^*$  constitutes a Hermitian matrix, when arranged in a square array. This is the density matrix which we define as

$$\varrho_{nm} = \langle U^{(mn)} \rangle = \langle U^{(nm)} \rangle^*. \quad (3)$$

The order of the indices of  $\varrho$  is chosen so that (1) may be written in the condensed form

$$\langle A \rangle = \sum_{mn} A_{mn} \varrho_{nm} = \text{Tr}(A\varrho). \quad (4)$$

The approach to the density matrix followed here and in ref. (1) has been called the “operational” point of view (6).

### B. THE DENSITY MATRIX AS A STATE VECTOR

Any set of independent parameters related to the  $\langle U^{(mn)} \rangle = \varrho_{nm}$  by a transformation that possesses an inverse can serve to identify the state of the system and to calculate the mean values of all its operators in analogy to Eqs. (1) and (4). Such a set need not be ordered into a square array but can be laid out in a column and treated as the set of components of a state vector.

In the Liouville representation we consider in general a set of operators  $U^{(j)}$  and identify the state of a system through the set of mean values

$$\varrho_j = \langle U^{(j)\dagger} \rangle = \langle U^{(j)} \rangle^* = \sum_{mn} U^{(j)}_{mn}^* \varrho_{nm}. \quad (5)$$

We shall assume for convenience — unless otherwise stated and although this assumption is unnecessary — that the set of operators is orthonormalized, in the sense that

$$\text{Tr} \{ U^{(j)} U^{(k)\dagger} \} = \delta_{jk}. \quad (6)$$

This convention implies that the set of all matrix elements  $U^{(j)}_{mn}$ , arranged in a rectangular array with the row index  $j$  and the column index  $(m, n)$ , constitutes a square unitary matrix. The simplest and most familiar example of this procedure consists of the replacement of a

$2 \times 2$  spin orientation (or light polarization) density matrix by the mean values of the 4 operators  $I/\sqrt{2}$ ,  $\sigma_x/\sqrt{2}$ ,  $\sigma_y/\sqrt{2}$ ,  $\sigma_z/\sqrt{2}$ , where  $I$  indicates the unity matrix and  $\sigma_x$ ,  $\sigma_y$ ,  $\sigma_z$  the Pauli spin matrices.

The operators  $U^{(j)}$  can then be regarded as unit coordinate vectors of a vector space in which all operators are represented by the general formula

$$\mathbf{A} = \sum_j A_j^* \mathbf{U}^{(j)} = \sum_j A_j \mathbf{U}^{(j)\dagger}. \quad (7a)$$

The state vector representation is then a particular case of Eq. (7a), namely

$$\rho = \sum_j \varrho_j^* \mathbf{U}^{(j)} = \sum_j \varrho_j \mathbf{U}^{(j)\dagger}. \quad (7b)$$

The vector components in Eqs. (7a) and (7b) are

$$A_j = \text{Tr}(AU^{(j)}) = \mathbf{A} \cdot \mathbf{U}^{(j)}, \quad \varrho_j = \text{Tr}(\varrho U^{(j)}) = \rho \cdot \mathbf{U}^{(j)} \quad (8)$$

and a generalized form of Eq. (4) is

$$\langle A \rangle = \text{Tr}(A\rho) = \sum_j A_j \varrho_j^* = \sum_j A_j^* \varrho_j = \mathbf{A} \cdot \rho, \quad (9)$$

where the trace of a product of operators has taken the form of a scalar product of vectors.

The operators  $U^{(j)}$  can always be chosen Hermitian, since a non-Hermitian  $U$  and its conjugate  $U^\dagger$  can be replaced by Hermitian combinations  $U + U^\dagger$  and  $i(U - U^\dagger)$ . In this event the  $\varrho_j$  are *real* and can be regarded as cartesian components of a real state vector  $\rho$ . From this standpoint the use of a non-Hermitian operator, such as the combinations of Pauli matrices  $\sigma_x \pm i\sigma_y$ , corresponds to the representation of a real  $\rho$  in terms of complex cartesian components. This complex representation constitutes merely an analytical device analogous to the representation of a position vector  $\mathbf{r}$  in terms of  $x \pm iy$  and  $z$ , or to a Fourier expansion in terms of complex exponentials instead of sines and cosines. Here we shall assume the  $U^{(j)}$  to be Hermitian and the  $\varrho_j$  real, unless otherwise noted, thus achieving a more immediate relation between the state representation and real, observable, physical quantities.

### C. LIMITATIONS TO THE VECTOR $\rho$

The unity operator  $I$  has the mean value 1 whatever be the state of a system. Therefore, choosing one of the  $U^{(j)}$  proportional to  $I$ ,

$$U^{(0)} = I [\text{Tr } I]^{-1/2}, \quad (10)$$

yields advance knowledge of the corresponding component of  $\rho$ ,

$$\varrho_0 = [\text{Tr } I]^{-1/2}. \quad (11)$$

The state is thus seen to be actually identified by the set of components of  $\rho$  *exclusive of*  $\varrho_0$ . This smaller set, which identifies a vector orthogonal to  $I$ , will be called the *special Liouville representation* of the state. It consists of mean values of operators  $U^{(j)}$  with trace zero, owing to (6).

The density matrix  $\varrho_{mn}$  of any state can be reduced to a diagonal form  $\varrho_{\alpha\beta} = \varrho_a \delta_{\alpha\beta}$  which is indicated, in the Liouville representation, by

$$\rho = \sum_a p_a \rho^{(a)}. \quad (12)$$

Here the  $\rho^{(a)}$  are the eigenvectors of  $\varrho$ , which form an orthonormalized system in the sense that

$$\rho^{(a)} \cdot \rho^{(\beta)} = \delta_{a\beta}. \quad (13)$$

Notice that the eigenvalues  $p_a$  of the matrix  $\varrho_{mn}$  must be nonnegative in order that any operator with nonnegative eigenvalues have a nonnegative mean value. In the notation of (2) the  $\rho^{(a)}$  are designated as  $U^{(aa)}$ . From Eqs. (11) and (13), and from the condition  $p_a \geq 0$  follows

$$\sum_a p_a = 1 \quad (14)$$

$$\sum_a p_a^r = \text{Tr} (\varrho^r) \leq 1, \quad r > 1. \quad (15a)$$

Equation (15a) is particularly important for  $r = 2$ , since it limits the length of the vector  $\rho$ ,

$$\sum_a p_a^2 = \text{Tr} (\varrho^2) = \rho \cdot \rho \leq 1. \quad (15b)$$

The upper limit 1 in Eqs. (15a) and (15b) is attained for pure states, in which case one of the  $p_a$  equals 1 and the others vanish.

### D. SYMMETRIES AND PROJECTIONS

States of many-body systems, and often also of simple systems, are generally characterized by a number of parameters far smaller than the dimensionality of the vector space  $\rho$ . This means that the characterization of  $\rho$  is then completed by implied statements. Often, very large classes of components of  $\rho$  are thus implied to vanish for reasons of symmetry. For example, if a spinning particle is oriented by an axially symmetric field or other mechanism, all operators that vary sinusoidally under rotations about the symmetry axis have mean values equal to zero. Systems in thermal equilibrium have zero mean values for all operators that are orthogonal — in the sense of Eq. (6) — to all powers of the Hamiltonian; the thermodynamic equations

$$\langle H^n \rangle = [\langle H \rangle - d/d(1/kT)]^{n-1} \langle H \rangle$$

specify  $\rho$  further.

Again, when dealing with complex systems, one is usually interested in determining the mean values of only a few operators. Indeed, one could not even examine the mean values of the huge number of possible operators even if they were provided by a machine. In the Liouville representation the mean values of the operators of interest characterize the projection of  $\rho$  on a very small subspace of the entire space of state vectors. This geometric interpretation is of help in describing the nature of irreversibility and relaxation.

### E. THE EQUATION OF MOTION

The Schrödinger-von Neumann equation of motion for density matrices,

$$d\rho/dt = -i\hbar^{-1} (H\rho - \rho H), \quad (16)$$

conserves the value of  $\text{Tr}(\rho^2)$  in Eq. (15a). In particular it conserves  $\text{Tr}(\rho^2) = \rho \cdot \rho$ , the length  $\rho$ , and therefore represents an infinitesimal rotation of the vector space. Accordingly it can be represented in the alternative notations

$$d\rho/dt = \mathbf{R}\rho = -i\mathbf{L}\rho, \quad (17)$$

where  $\mathbf{R}$  and  $\mathbf{L}$  are operators of the vector space,  $\mathbf{L}$  is Hermitian and

**R** anti-Hermitian, and the eigenvalues of **L** are either of equal modulus and opposite sign in pairs or else equal to zero. In terms of real cartesian coordinates of the vector space, **R** is represented by a real skew-symmetric matrix. The eigenvectors of **L** are the non-Hermitian operator  $\mathbf{U}^{(rs)}$ , where  $r$  and  $s$  indicate eigenstates of the Hamiltonian, and the corresponding eigenvalues are the proper frequencies

$$\omega_{rs} = (E_r - E_s)/\hbar \quad (18)$$

of the system. Notice that the directly observable frequencies appear in this representation rather than the indirectly determined energy levels.

The simplest example of Eq. (17) pertains to the state of orientation of a spin- $\frac{1}{2}$  particle

$$d\langle \boldsymbol{\sigma} \rangle / dt = -\gamma \mathbf{H} \times \langle \boldsymbol{\sigma} \rangle \quad (19)$$

and describes the Larmor precession of the mean spin vector about the magnetic field **H** at the rate of  $\gamma H$  radian/sec. [ $\gamma$  = gyromagnetic ratio, the operator **R** is represented by  $-\gamma \mathbf{H} \times$  and a factor  $1/\sqrt{2}$  should be added to match the normalization of (17).]

In the limiting case of a classical system with canonical coordinates  $q_i$  and  $p_i$ , in which

$$\mathbf{p} \rightarrow f(q_i, p_i), \quad \mathbf{R} \rightarrow \sum_i \left[ \frac{\partial H}{\partial q_i} \frac{\partial}{\partial p_i} - \frac{\partial H}{\partial p_i} \frac{\partial}{\partial q_i} \right], \quad (20)$$

equation (17) reduces to the Liouville equation for the distribution function  $f(q_i, p_i)$ . Hence comes the name of our vector space representation.

The explicit form of **L** and **R** is obtained by comparing Eqs. (17) and (16) in the representation with coordinate axes  $\mathbf{U}^{(mn)}$  and components  $\varrho_{mn}$

$$\begin{aligned} L_{mn, m'n'} &= \hbar^{-1} [H_{mm'} \delta_{nn'} - H_{n'n} \delta_{mm'}] \\ &= \hbar^{-1} [H_{mm'} \delta_{nn'} - \delta_{mm'} H_{nn'}^*]. \end{aligned} \quad (21a)$$

One can write more compactly

$$\mathbf{L} = \hbar^{-1} (HI^* - IH^*), \quad (21b)$$

where the operator products on the right are direct products of the

Hamiltonian and of the unity operator pertaining to different indexes. The explicit form of  $\mathbf{L}$  in a representation with axes  $\mathbf{U}^{(j)}$  is obtained from Eq. (20) by means of the transformation formula (5) and of its inverse.

The equation of motion (17) has the formal solution

$$\rho(t) = \exp(\mathbf{R}t) \rho(0) = \exp(-i\mathbf{L}t) \rho(0). \quad (22)$$

Equation (17) and its solution (22) determine by implication the variation in the course of time of whatever projection of  $\rho$  may be of interest. Of course, the variation of a projection within a subspace *does not constitute a rotation*, in general when the full vector  $\rho$  rotates. Even though the quantities  $\text{Tr}(\rho')$  pertaining to the full density matrix are conserved, corresponding quantities pertaining to a projection are not. By the same token, even though knowledge of  $\rho(t)$  at the time  $t$  implies, by inversion of Eq. (22), what the state had been at  $t = 0$ , knowledge of a projection of  $\rho(t)$  does *not* determine what the corresponding projection had been at  $t = 0$ . Irreversibility, in this restricted sense, thus appears self-evident.

One may anticipate that, in phenomena involving dissipation and relaxation, the projection of  $\rho$  on the subspace of interest will approach a limit that represents a minimum of information, and in particular that the magnitude of this projection will decrease. At the moment we know only that this magnitude is not a constant of the motion. It is an open problem, discussed further in Section II, to define the physicomathematical conditions that lead to a dissipative behavior.

#### F. FOURIER TRANSFORMATION

The time variation of the state vector  $\rho(t)$  can be represented as a superposition of harmonic components by the Fourier integral

$$\rho(t) = -\frac{1}{2\pi i} \int_{-\infty+i\varepsilon}^{\infty+i\varepsilon} d\omega \exp(-i\omega t) \rho(\omega), \quad (23)$$

where

$$\rho(\omega) = -i \int_0^\infty \exp(-i\omega t) \rho(t) dt = \frac{1}{\omega - \mathbf{L}} \rho(0), \quad \text{Im } \omega = \varepsilon > 0. \quad (24)$$

Study of the transform  $\rho(\omega)$ , of the formal solution (22), and of the

equation of motion (17) are equivalent, in principle. In practice, study of the formal solution for macroscopic times  $t$ , or, correspondingly, of the transform for rather low frequencies  $\omega$ , makes it unnecessary to consider transients over microscopic times or to eliminate them by "coarse-graining" the equation of motion explicitly. Moreover, study of  $\rho(\omega)$  enables one to treat memory effects algebraically as will be seen in Section II, rather than by convolution integrals over the time variable.

If one transformed the formal solution of (16), namely,  $\varrho(t) = \exp(-iHt/\hbar) \varrho(0) \exp(iHt/\hbar)$ , rather than (22), he would find

$$\varrho(\omega) = -\frac{1}{2\pi i} \int d\omega' \frac{1}{\omega - \omega' - iH/\hbar} \varrho(0) \frac{1}{\omega' + iH/\hbar} \quad (25)$$

instead of (24). The notation of the Liouville representation enables one, in effect, to reduce formally the integral in Eq. (25) to the residue around the pole at  $\omega' = -H/\hbar$ . The Van Hove treatment of many-body problems (7) deals in effect with the two-energy quantity in the integrand of Eq. (25).

#### G. ADDITIONAL FEATURES <sup>1</sup>

The relationship between the ordinary Hilbert space representation of quantum mechanics and the Liouville representation is well known in group theory. In the (complex) Hilbert space representation, (a) unit vectors represent pure states; (b) Hermitian operators represent physical quantities; (c) Hermitian operators with unit trace and nonnegative eigenvalues represent mixed states; and (d) unitary transformations carry alternative complete sets of orthogonal states into one another. The group of these unitary transformations represents the group of quantum mechanical transformations that relate the sets of eigenstates of incompatible physical quantities. The (real) Liouville representation constitutes another representation of the same group of quantum mechanical transformations, which is called the *adjoint representation* of the group (8). The manifold of Hermitian operators of the ordinary Hilbert (unitary) representation corresponds to the manifold of all vectors of the Liouville (adjoint) representation.

<sup>1</sup> This section is unrelated to the following ones.

The unitary transformations of the Hilbert space include the operation  $\exp(i\varphi) I$  which renormalizes all vectors by a common phase factor  $\exp(i\varphi)$  and which represents no physical operation. (This operation differs from the gauge transformations which renormalize different position eigenvectors by different phase factors.) Any unitary transformation can be factored into a unimodular transformation matrix, with determinant equal to unity, and a physically meaningless  $\exp(i\varphi) I$ . The group of quantum mechanical transformations is actually represented by the “special unitary” group (SU) which includes only unimodular transformations. No transformation in the Liouville representation corresponds to the unphysical transformation  $\exp(i\varphi) I$ . However, exclusion of this transformation corresponds to the fact that the Liouville vector  $\mathbf{U}^{(0)}$ , Eq. (10), is invariant under all transformations of the Liouville representation and that these transformations are confined to the “special Liouville representation” (Section II, C) which contains only vectors orthogonal to  $\mathbf{U}^{(0)}$ .

A complete set of orthogonal states of a quantum mechanical system is represented, according to (13), by a set of orthogonal unit vectors  $\rho^{(\alpha)}, \rho^{(\beta)}, \dots$  of the Liouville representation. If these vectors fan out of the origin of coordinates, their tips lie on the hyperplane defined by Eq. (11), which contains the special Liouville representation, and form within this hyperplane a geometrical figure called a “simplex.” A two-dimensional simplex is an equilateral triangle, a three-dimensional one is a regular tetrahedron, etc.) The tips of state vectors  $\rho$  corresponding to mixed states lie within or on the boundaries of a simplex, according to Eq. (12).

The group of transformations that relate different complete sets of pure states  $\rho^{(\alpha)}, \rho^{(\beta)}, \dots$  and  $\rho^{(\mu)}, \rho^{(\nu)}, \dots$  is represented by a subgroup of rotations of the Liouville representation. This subgroup must be such that

$$\rho^{(\alpha)} \cdot \rho^{(\mu)} \geq 0 \quad \text{for all pairs } (\alpha, \mu) \quad (26)$$

because this product represents the probability of finding the system in the state  $\mu$  if it was known to be in the state  $\alpha$ . To characterize this subgroup, recall that each unitary transformation of the Hilbert space representation can be generated by a sequence of two-dimensional transformations. Thus we can start by replacing  $\rho^{(\alpha)}$  and  $\rho^{(\beta)}$  with a new pair

$\rho^{(\alpha)}$ ,  $\rho^{(\beta)}$ , leaving all other eigenstates  $\rho^{(\gamma)}$ , ... fixed. Later on, the most general Liouville transformation can be generated by a sequence of transformations of pairs of eigenstates. Let us represent the pair  $(\alpha, \beta)$  in the form

$$\rho^{(\alpha, \beta)} = \frac{1}{2} [\rho^{(\alpha)} + \rho^{(\beta)}] \pm \frac{1}{2} [\rho^{(\alpha)} - \rho^{(\beta)}] \quad (27)$$

where the vectors  $[\rho^{(\alpha)} + \rho^{(\beta)}]/2$  and  $[\rho^{(\alpha)} - \rho^{(\beta)}]/2$  have length  $1/\sqrt{2}$  and are mutually orthogonal and orthogonal to all other vectors  $\rho^{(\gamma)}$ ,  $\rho^{(\delta)}$  ... of the set. The basic conditions (13) and (26) are then met by taking as new state vectors

$$\rho^{(\alpha', \beta')} = \frac{1}{2} [\rho^{(\alpha)} + \rho^{(\beta)}] \pm \mathbf{q} \quad (28)$$

where  $\mathbf{q}$  is another vector of length  $1/\sqrt{2}$  orthogonal to  $[\rho^{(\alpha)} + \rho^{(\beta)}]/2$  and to all  $\rho^{(\gamma)}, \rho^{(\delta)}$  .... That is, the tips of  $\rho^{(\alpha')}$  and  $\rho^{(\beta')}$  lie on opposite poles of a sphere of which  $[\rho^{(\alpha)} - \rho^{(\beta)}]/2$  is a diameter. Reference to the  $2 \times 2$  Hilbert space transformations from  $(\alpha, \beta)$  to  $(\alpha', \beta')$  or to the example of the pairs of orientation states of a spin-1/2 particle shows that we deal here in fact with a sphere of a three-dimensional space of vectors  $\mathbf{q}$ . In other words any pair  $(\alpha', \beta')$  is identified by two parameters which specify the orientation of  $\mathbf{q}$ .

Two choices of  $\mathbf{q}$ , mutually orthogonal and orthogonal to  $[\rho^{(\alpha)} - \rho^{(\beta)}]/2$ , are

$$\frac{1}{2} [\mathbf{U}^{(\alpha\beta)} + \mathbf{U}^{(\beta\alpha)}], \quad \frac{1}{2} [\mathbf{U}^{(\alpha\beta)} - \mathbf{U}^{(\beta\alpha)}]. \quad (29)$$

The set of pairs of these vectors, for all pairs of states  $(\alpha, \beta)$ ,  $(\alpha, \gamma)$ ,  $(\beta, \gamma)$ , ect., renormalized by a factor  $\sqrt{2}$ , together with the initial set of  $\rho^{(\alpha)} = \mathbf{U}^{(\alpha\alpha)}$  constitutes a complete set of  $\mathbf{U}^{(ij)}$  spanning the whole Liouville representation. Any operator representative  $\mathbf{A}$  can be expanded in terms of this set, according to Eq. (7a).

The ordinary diagonalization procedure of the Hermitian matrix  $A_{mn}$ , the Hilbert space representative of a physical quantity, corresponds to a reduction of the Liouville representative  $\mathbf{A}$  to the form

$$\mathbf{A} = \sum_{\mu} A_{\mu} \rho^{(\mu)}, \quad (30)$$

where the  $\rho^{(\mu)}$  are the eigenstates and  $A_{\mu}$  the eigenvalues of  $A$ . The direction of the vector  $\mathbf{A}$  thus identifies one orthonormal set of pure

state vectors, except in the case of degeneracy in which there are many such sets with common elements and having  $\mathbf{A}$  as a common symmetry axis.

Equation (30) emphasizes that the state vector  $\rho^{(\mu)}$  coincides with the representative vector  $\mathbf{P}^{(\mu)}$  of a quantity which has  $\rho^{(\mu)}$  as an eigenstate with the eigenvalue 1 and has all other eigenvalues equal to zero. This quantity is accordingly represented by a projection operator of the Hilbert space. Indeed, the procedure for measuring  $\mathbf{P}^{(\mu)}$  coincides with the procedure for selecting systems in the state  $\rho^{(\mu)}$ . An arbitrary quantity  $A$  can then be regarded as a linear combination of  $\mathbf{P}^{(\mu)}$  with the eigenvalues  $A_\mu$  as coefficients.

It appears possible to develop all of quantum mechanics in the (real) Liouville representation directly through statements of experimental evidence, without any reference to the Hilbert space representation. The Hilbert space representation achieves, of course, analytical economy through its use of complex numbers. The economy is particularly evident in the representation of quantum mechanical transformations through unimodular matrices, because these matrices have far smaller dimensionality than those that represent the corresponding unfamiliar subgroup of rotations in the Liouville representation. The advantages of the Liouville representation lie in its unified treatment of pure and mixed states and of their time evolution, in its more direct representation of symmetries, of projections, of eigenvalues and mean values and, generally, in its closer relationship to experimental observations.

### III. Interaction with a Reservoir

The shift and broadening of the spectral lines of an atom due to collisions with surrounding gas molecules and the approach to thermal equilibrium of nuclear orientation due to coupling with a crystal lattice are among the numerous phenomena in which a system of interest experiences effects of interaction with a much larger system that acts as a noisy thermal reservoir. In macroscopic physics, situations of this kind are often treated adequately by schematizing the effect of the reservoir on the system of interest by a friction coefficient or other relaxation parameter. On the other hand, a microscopic, quantum mechanical

treatment must start from a Hamiltonian, nondissipative, formulation. This initial formulation must then regard the reservoir and the system of interest as forming together a single large conservative system. The manifold irrelevant details of the reservoir have to be eliminated in the course of the treatment.

Numerous problems have been treated along these lines in the last 10–15 years, a prototype being perhaps the Wangsness-Bloch theory of nuclear induction and relaxation (9). Semimicroscopic treatments have also been given, in which the system of interest is treated quantum mechanically but the effect of the reservoir upon it is represented schematically by fluctuating fields; the results depend then on autocorrelations of these fields which are regarded as phenomenological parameters.

This section presents a general procedure which starts from the full quantum mechanical formulation of system of interest + reservoir, then eliminates the irrelevant reservoir variables and obtains, in effect, an equation of motion for the system of interest with dissipative parameters akin to the macroscopic ones. We propose to point out the approximations involved in the procedure and the conditions that have to be met for the system of interest to behave according to the macroscopic concept of relaxation. However this program cannot be carried out completely at this time, because certain key points require further study, as will be seen. The procedure involves three formal steps, namely: A suitable representation of the interaction between system and reservoir, the characterization of the relevant properties of the initial state of the complete system, and the elimination of irrelevant variables. Thereby we shall obtain in Eq. (52), instead of the resolvent  $(\omega - \mathbf{L})^{-1}$  on the right-hand side of (24), which pertains to the complete system, a modified resolvent which pertains to the system of interest only. Only a few properties of this modified resolvent are known at this time.

#### A. THE TRANSITION OPERATOR

Consider a complete system, consisting of a part, called “system of interest,” with Hamiltonian  $H_s$  and of a larger reservoir, or thermal bath, with Hamiltonian  $H_b$ . Calling  $V$  the interaction between the two parts we write the Hamiltonian of the complete system as

$$H = H_s + H_b + V. \quad (31)$$

In accordance with (21a), the corresponding Liouville operator has the form

$$\mathbf{L} = \mathbf{L}_0 + \mathbf{L}_1 = \mathbf{L}_s + \mathbf{L}_b + \mathbf{L}_1, \quad (32a)$$

where

$$\mathbf{L}_s = H_s I_b (I_s I_b)^* - I_s I_b (H_s I_b)^*,$$

$$\mathbf{L}_b = I_s H_b (I_s I_b)^* - I_s I_b (I_s H_b)^*, \quad (32b)$$

$$\mathbf{L}_1 = V (I_s I_b)^* - I_s I_b V^*,$$

and the  $I$  are unity operators.

In preparation for the elimination of the bath variables it is convenient to disentangle the interaction term  $\mathbf{L}_1$  from the denominator of the resolvent operator. This is achieved by the operator identity

$$\frac{1}{\omega - \mathbf{L}_0 - \mathbf{L}_1} = \frac{1}{\omega - \mathbf{L}_0} \left[ 1 + \mathbf{M}(\omega) \frac{1}{\omega - \mathbf{L}_0} \right], \quad (33)$$

where  $\mathbf{M}(\omega)$  is a transition operator with the equivalent expressions

$$\begin{aligned} \mathbf{M}(\omega) &= \frac{1}{1 - \mathbf{L}_1 (\omega - \mathbf{L}_0)^{-1}} \mathbf{L}_1 = \mathbf{L}_1 \frac{1}{1 - (\omega - \mathbf{L}_0)^{-1} \mathbf{L}_1} \\ &= \mathbf{L}_1 + \mathbf{L}_1 \frac{1}{\omega - \mathbf{L}_0 - \mathbf{L}_1} \mathbf{L}_1 = \mathbf{L}_1 \sum_{n=0}^{\infty} \left[ \frac{1}{\omega - \mathbf{L}_0} \mathbf{L}_1 \right]^n. \end{aligned} \quad (34)$$

The name "transition operator" is suggested by the analogy between the equation

$$\mathbf{M}(\omega) = \mathbf{L}_1 + \mathbf{L}_1 \frac{1}{\omega - \mathbf{L}_0} \mathbf{M}(\omega) \quad (35)$$

satisfied by  $\mathbf{M}$  and the equation  $T = V + V(\omega - H_0)^{-1} T$  satisfied by the transition operator of the Lippman-Schwinger scattering theory. We are interested here primarily in the existence and general properties of  $\mathbf{M}$ , particularly in the fact that it embodies the effects of interaction between system and bath to all orders, rather than in its possible calculation by summing the perturbation series on the right of (34) or by solving Eq. (35).

The fact that  $\text{Im } \omega > 0$ , according to (24), classifies  $\mathbf{M}$  as a forward-

in-time transition operator. The non-Hermitian transition operators can be expressed in terms of corresponding Hermitian reaction operators, which are defined for real values of the energy parameter. To this end we separate the real and imaginary parts of  $\omega$  by setting

$$\omega = \omega' + i\epsilon \quad (36)$$

and apply the well-known formula

$$\lim_{\epsilon \rightarrow 0} \frac{1}{\omega' + i\epsilon - \mathbf{L}_0} = \mathcal{P} \frac{1}{\omega' - \mathbf{L}_0} - i\pi\delta(\omega' - \mathbf{L}_0), \quad (37)$$

where  $\mathcal{P}$  indicates that the Cauchy principal part is to be taken in integrations over the poles of  $(\omega' - \mathbf{L}_0)^{-1}$ . Substitution in (34) or (35) yields

$$\mathbf{M}(\omega' + i0) = \mathbf{N}(\omega')/[1 + i\pi\delta(\omega' - \mathbf{L}_0)\mathbf{N}(\omega')] \quad (38)$$

where  $\mathbf{N}(\omega')$  is a Hermitian reaction operator obtained by replacing  $\omega$  in the Eqs. (34) and (35) by  $\omega'$ :

$$\mathbf{N}(\omega') = \mathbf{L}_1 \frac{1}{1 - \mathcal{P}(\omega' - \mathbf{L}_0)^{-1} \mathbf{L}_1} = \mathbf{L}_1 + \mathbf{L}_1 \frac{\mathcal{P}}{\omega' - \mathbf{L}_0} \mathbf{N}(\omega'). \quad (39)$$

Equation (38) enables us to resolve  $\mathbf{M}(\omega' + i0)$  into an Hermitian and an anti-Hermitian operator,

$$\begin{aligned} \mathbf{M}(\omega' + i0) &= \mathbf{N}(\omega') \frac{1}{1 + [\pi\delta(\omega' - \mathbf{L}_0)\mathbf{N}(\omega')]^2} \\ &\quad - i\pi \mathbf{N}(\omega') \delta(\omega' - \mathbf{L}_0) \mathbf{N}(\omega') \frac{1}{1 + [\pi\delta(\omega' - \mathbf{L}_0)\mathbf{N}(\omega')]^2}. \end{aligned} \quad (40)$$

Notice that the imaginary part

$$\frac{1}{2} i[\mathbf{M}(\omega' + i0) - \mathbf{M}(\omega' + i0)^\dagger] = \pi \mathbf{M}(\omega' + i0) \delta(\omega' - \mathbf{L}_0) \mathbf{M}(\omega' + i0)^\dagger \quad (41)$$

is *non negative*. (Equation (41) also follows from the statement that  $1 + 2\pi i \mathbf{M}(\omega' + i0) \delta(\omega' - \mathbf{L}_0)$  constitutes a unitary scattering operator.)

### B. THE INITIAL STATE OF THE COMPLETE SYSTEM

The density matrix  $\varrho$  of the complete system, at an initial time  $t = 0$ , contains information on the state of the system of interest, on the state of the reservoir, and on the correlations between variables of system and reservoir. The information about either part of the complete system is extracted from  $\varrho$  by summing over the variables of the other part. Specifically, we may consider a set of eigenstates  $u_\mu, u_\nu, \dots$  of the Hamiltonian  $H_s$  of the system of interest and a set of eigenstates  $v_\alpha, v_\beta, \dots$  of the reservoir Hamiltonian  $H_b$ . The products  $u_\mu v_\alpha, u_\nu v_\beta, \dots$  constitute a complete set of states of the complete system. In this representation, the density matrix has the elements  $\varrho_{\mu\alpha, \nu\beta}$ . Density matrices for "system" and "bath" are obtained from  $\varrho$  in the form

$$\varrho^{(s)} = \text{Tr}_b \varrho, \quad \text{i.e.,} \quad \varrho_{\mu\nu}^{(s)} = \sum_a \varrho_{\mu a, \nu a}, \quad (42a)$$

$$\varrho^{(b)} = \text{Tr}_s \varrho, \quad \text{i.e.,} \quad \varrho_{\alpha\beta}^{(b)} = \sum_\mu \varrho_{\mu\alpha, \mu\beta}. \quad (42b)$$

In the Liouville representation one may consider a complete set of operator products with matrice  $U_{\mu\rho}^{(j)} V_{\alpha j}^{(\tau)}$ , in which  $U^{(0)}$  is proportional to the unity operator  $I_s$  and  $V^{(0)}$  to  $I_b$ . The components  $\varrho_{\cdot 0}$  of  $\varrho$  provide then the same information as  $\varrho^{(s)}$ , the  $\varrho_0$ , the same as  $\varrho^{(b)}$ . In fact, the projection of  $\varrho$  on the subspace corresponding to the components  $\varrho_{\cdot 0}$  may be indicated by  $\varrho^{(s)} [\text{Tr } I_b]^{-1/2}$ , i.e., coincides with  $\varrho^{(s)}$  to within a normalization factor.

The concept of a reservoir corresponds to the statement that  $\varrho^{(b)}$  represents a state of thermal equilibrium — i.e.,  $\varrho^{(b)} = \exp(-H_b/kT)/[\text{Tr}\{\exp(-H_b/kT)\}]$  — or at least a steady state, such that  $\varrho^{(b)}$  commutes with  $H_b$  and that in the Liouville representation

$$\mathbf{L}_b \varrho^{(b)} = 0. \quad (43)$$

In the following we assume that Eq. (43) holds at the initial time  $t = 0$ . On the other hand no special statement regarding  $\varrho^{(s)}$  at  $t = 0$  is relevant to our discussion and, therefore, we leave  $\varrho^{(s)}$  unspecified.

Proceeding now to the correlations between the system of interest and the reservoir, we recall from Section 3h of ref. (I) that the mean value of the product of any two physical variables of *uncorrelated* systems

equals the product of the respective mean values. This is to say that  $\langle U^{(j)} V^{(r)} \rangle = \langle U^{(j)} \rangle \langle V^{(r)} \rangle$ , or

$$\varrho_{jr} = \varrho_{,0} \varrho_{0r} / \varrho_{00} \quad (\text{no correlation}), \quad (44)$$

or  $\varrho = \varrho^{(s)} \varrho^{(b)}$ . Out of any given initial  $\varrho(0)$  one can extract its uncorrelated part by a projection operation. Zwanzig has pointed out that, in a number of cases, the relevant projection operator  $P$  is conveniently defined by

$$PA = \varrho^{(b)}(0) \operatorname{Tr}_b \{A\}, \quad (45a)$$

that is,

$$(PA)_{\mu a, \nu \beta} = \varrho^{(b)}(0)_{a\beta} \sum_{a'} A_{\mu a', \nu a'}. \quad (45b)$$

Application of Eq. (45a) to  $A = \varrho(0)$  yields

$$P\varrho(0) = \varrho^{(s)} \varrho^{(b)}(0), \quad (46a)$$

that is

$$(P\varrho(0))_{jr} = \varrho_{,0} \varrho_{0r} / \varrho_{00}. \quad (46b)$$

Correlations between the system of interest and the reservoir are of essence in their interaction process. On the other hand, it is inherent in the concept of a reservoir that its influence on the system of interest depends on steady state properties of the reservoir alone rather than on preexisting correlations between the reservoir and the system of interest. To realize this concept it is sufficient to assume that the *initial correlations*, represented by  $(1 - P)\varrho(0)$ , *have no appreciable effect* on the system of interest over relevant intervals of time which are not very short. In the problem of pressure broadening of spectral lines in a gas this assumption holds to lowest order in the gas density. In general, however, this assumption is neither necessary nor realistic. It is still unclear how one should embody appropriately the relevant properties of a reservoir in the statement of our problem. As an interim procedure, for the remainder of this lecture, we shall assume

$$(1 - P) \varrho(0) \sim 0 \quad (47)$$

with  $P$  defined by (45).

### C. ELIMINATION OF RESERVOIR VARIABLES

We are concerned, in our study, with the state of the system of interest at times  $t > 0$ , that is, with  $\varrho^{(s)}(t)$  or, equivalently, with

$$\varrho^{(s)}(\omega) = \text{Tr}_b \{ \mathbf{\rho}(\omega) \}, \quad (48a)$$

whose elements are  $\varrho_{\mu\nu}^{(s)} = \sum_a \varrho_{\mu a, \nu a}(\omega)$ . The summation over the states  $a$  of the reservoir eliminates the irrelevant variables. In the Liouville representation, this operation constitutes a projection of the vector  $\mathbf{\rho}$  onto the subspace with components  $\varrho_{,0}$ , in the sense of Section I, D, and may be expressed in the form

$$\mathbf{\rho}^{(s)}(\omega) = \mathbf{I}_b \cdot \frac{1}{\omega - \mathbf{L}} \mathbf{\rho}(0). \quad (48b)$$

(Notice, incidentally, that the operator  $P$  defined by Eq. (45) involves this projection as an intermediate step but generates a vector that does not lie in the subspace of the  $\varrho_{,0}$ .)

To bring (48b) to a more compact form, we take the resolvent  $(\omega - \mathbf{L})^{-1}$  in the form (33) and replace  $\varrho(0)$  with  $P\varrho(0)$  in accordance with Eq. (47), which yields

$$\mathbf{\rho}^{(s)}(\omega) = \mathbf{I}_b \cdot \frac{1}{\omega - \mathbf{L}_0} \left[ 1 + \mathbf{M}(\omega) \frac{1}{\omega - \mathbf{L}_0} \right] \varrho^{(b)}(0) \mathbf{\rho}^{(s)}(0). \quad (49)$$

It follows from Eq. (43) that  $\mathbf{L}_0 \varrho^{(b)}(0) = \varrho^{(b)}(0) \mathbf{L}_s$ . Similarly we have  $I_b \mathbf{L}_0 = \mathbf{L}_s I_b$  because  $I_b$  commutes with the Hamiltonian  $H_b$ . Thereby (49) reduces to

$$\mathbf{\rho}^{(s)}(\omega) = \frac{1}{\omega - \mathbf{L}_s} \left[ 1 + \langle \mathbf{M}(\omega) \rangle \frac{1}{\omega - \mathbf{L}_0} \right] \mathbf{\rho}^{(s)}(0), \quad (50)$$

in which all effects of interaction with the reservoir are condensed in the operator of the system of interest

$$\langle \mathbf{M}(\omega) \rangle = \mathbf{I}_b \cdot \mathbf{M}(\omega) \cdot \varrho^{(b)}(0) = \text{Tr}_b \{ \mathbf{M}(\omega) \varrho^{(b)}(0) \}. \quad (51)$$

Finally, (50) can be reduced to the form of a resolvent operating on  $\mathbf{\rho}^{(s)}(0)$  by “reentangling”  $\langle \mathbf{M}(\omega) \rangle$  with  $\mathbf{L}_s$ . This is achieved by applying

the identity (33)–(34) in reverse, to yield the main result (2)

$$\rho^{(s)}(\omega) = \frac{1}{\omega - \mathbf{L}_s - \langle \mathbf{M}_c(\omega) \rangle} \rho^{(s)}(0) \quad (52)$$

with

$$\langle \mathbf{M}_c(\omega) \rangle = \frac{1}{1 + \langle \mathbf{M}(\omega) \rangle (\omega - \mathbf{L}_0)^{-1}} \langle \mathbf{M}(\omega) \rangle = \langle \mathbf{M} \rangle \sum_{n=0}^{\infty} \left[ \frac{1}{\omega - \mathbf{L}_0} \langle \mathbf{M} \rangle \right]^n. \quad (53)$$

The operator  $\mathbf{M}_c(\omega)$  was introduced by Zwanzig through the formal expression

$$\mathbf{M}_c(\omega) = \frac{1}{1 - \mathbf{L}_1(1 - P)(\omega - \mathbf{L}_0)^{-1}} \mathbf{L}_1 = \mathbf{L}_1 \sum_{n=0}^{\infty} \left[ \frac{1 - P}{\omega - \mathbf{L}_0} \mathbf{L}_1 \right] \quad (54)$$

and the equation

$$\mathbf{M}_c(\omega) = \mathbf{L}_1 + \mathbf{L}_1 \frac{1 - P}{\omega - \mathbf{L}_0} \mathbf{M}_c(\omega), \quad (55)$$

which differ, respectively, from the corresponding formulas for  $M(\omega)$ , (34) and (35), only by the introduction of the operator  $1 - P$ . The presence of this operator in the perturbation expansion on the right of (54) shows it to have the character of a linked-diagram expansion. Similarly, the expansion reciprocal to (53)

$$\langle \mathbf{M}(\omega) \rangle = \langle \mathbf{M}_c(\omega) \rangle \sum_n \left[ \frac{1}{\omega - \mathbf{L}_s} \langle \mathbf{M}_c(\omega) \rangle \right]^n = \langle \mathbf{M}_c \rangle \sum_n \left[ \frac{P}{\omega - \mathbf{L}_0} \langle \mathbf{M}_c \rangle \right]^n \quad (56)$$

represents the construction of the general operator  $\langle \mathbf{M} \rangle$  as a sum of powers of linked-diagram or “connected” operators  $\langle \mathbf{M}_c \rangle$ . (Hence originates the subscript of the symbol  $\mathbf{M}_c$ .)

#### D. DIAGONALIZATION OF THE RESOLVENT

In the absence of interaction with the reservoir, i.e., for  $\langle \mathbf{M}_c \rangle = 0$ , the resolvent in (52) has eigenvalues  $(\omega - \omega_{\mu\nu})^{-1}$  according to Eq. (18). The time variations of  $\rho^{(s)}(t)$  are then represented by a superposition of harmonic oscillations (more precisely of complex exponentials) with the characteristic frequencies  $\omega_{\mu\nu}$  of the system of interest. Similarly,

for  $\langle \mathbf{M}_c \rangle \neq 0$ , the variations of  $\varrho^{(s)}(t)$  are represented by a superposition of exponentials if the resolvent  $(\omega - \mathbf{L}_s - \langle \mathbf{M}_c(\omega) \rangle)^{-1}$  can be diagonalized. The possibility of this diagonalization is not obvious, in general, because  $\langle \mathbf{M}_c(\omega) \rangle$  is not Hermitian.

On the other hand, the empirical fact that numerous physical variables relax through harmonic oscillations indicates that relevant conditions exist under which  $\mathbf{L}_s + \langle \mathbf{M}_c(\omega) \rangle$  has a diagonal form with eigenvalues  $\omega_j$ . The oscillation amplitude would diverge unless  $\text{Im } \omega_j \leq 0$ , that is, unless  $i(\langle \mathbf{M}_c(\omega) \rangle - \langle \mathbf{M}_c(\omega) \rangle^\dagger)$  is a nonnegative matrix. At present, we know from (41) that  $i(\mathbf{M}(\omega' + i0) - \mathbf{M}(\omega' + i0)^\dagger)$  is nonegative; note, however, that the elimination of reservoir variables is represented by the unsymmetric operation (51) which, in general, does not preserve the Hermitian character of a Liouville operator.

### E. RAYLEIGH-SCHRÖDINGER APPROXIMATION

The ordinary perturbation treatment of interactions in quantum mechanics does not apply directly to the coupling of the system of interest with a reservoir because the reservoir's spectrum is continuous. It applies, however, after elimination of the reservoir variables if the spectrum of the Liouville operator  $\mathbf{L}_s$  is discrete and is perturbed weakly by the interaction operator  $\langle \mathbf{M}_c(\omega) \rangle$ .

One utilizes here the scheme of eigenstates  $u_\mu, u_\nu, \dots$  of  $H_s$  in which  $\mathbf{L}_s$  is diagonal with the eigenvalues  $\omega_{\mu\nu}$ . The condition of applicability of the perturbation treatment is then the familiar one

$$\left| \frac{\langle \mathbf{M}_c(\omega) \rangle_{\mu\nu, \mu'\nu'}}{\omega_{\mu\nu} - \omega_{\mu'\nu'}} \right| \ll 1, \quad \text{for } (\mu, \nu) \neq (\mu', \nu'). \quad (57)$$

Often, as in the case of pressure broadening at low pressures, the lowest order of approximation is adequate, in which the perturbation of the eigenvectors of  $\mathbf{L}_s$  is disregarded and the eigenvalues  $\omega_{\mu\nu}$  are replaced by

$$\omega_{\mu\nu} + \langle \mathbf{M}_c(\omega_{\mu\nu}) \rangle_{\mu\nu, \mu\nu} \quad (58)$$

The real and imaginary parts of the  $\mu\nu, \mu\nu$  diagonal matrix element  $\langle \mathbf{M}_c \rangle_{\mu\nu, \mu\nu}$  represent then the shift and broadening of the characteristic frequency  $\omega_{\mu\nu}$ .

Even when the condition (56) is valid for most of the spectrum of  $\mathbf{L}_s$ , it breaks down for groups of degenerate or quasi-degenerate eigenvalues. The preliminary zero-order approximation step is then required in which one diagonalizes exactly the relevant submatrices of the resolvent  $[\omega - \mathbf{L}_s - \langle \mathbf{M}_c(\omega) \rangle]^{-1}$ . In particular, degeneracy always occurs for the set of zero eigenvalues of  $\mathbf{L}_s$  whose eigenvectors are the diagonal operators  $U^{(\mu\mu)}$ . Slow relaxation, unaccompanied by oscillations, usually corresponds to these zero eigenvalues.

#### F. LOW-DENSITY APPROXIMATION

The effect of interaction with a reservoir is weak and amenable to approximate treatment when the interaction proceeds through a sequence of collision processes sufficiently separated in time from one another. This situation occurs in the pressure shift and broadening of spectral lines in a gas when the gas density is not too high and in solid state phenomena due to interaction with a low concentration of impurities. It is understood here that the interaction with each gas molecule or impurity is not necessarily weak and is not to be treated by perturbation methods. Nevertheless, the aggregate effect of the interaction on the system of interest is small in the limit of low concentration of gas molecules or of impurities and is appropriately represented by an expansion into powers of this concentration.

This expansion has been treated in Sections 4 and 5 of (5). The coefficients of the successive powers of the concentration are expressed in terms of single-collision parameters which are accessible in principle — and, to some extent, in practice — to direct calculation or experimental determination. The combination of single-scattering parameters increases in complexity very rapidly with the order of the coefficient, but the first coefficient, which is of greatest importance, is rather simple.

#### G. SHORT-MEMORY EXPANSION

The effects of interaction with a reservoir are also weak and amenable to approximate calculation when they dissipate rapidly through the reservoir. This situation occurs presumably in nuclear spin relaxation, where each nuclear spin is effectively coupled only to the electron

spins and to the positions of adjacent atoms, these variables being in turn coupled to those of farther atoms and so on. The collectivity of lattice atoms acts as a reservoir. Because of the rapid propagation of disturbances through the lattice, the variables of atoms adjacent to any one nuclear spin remain correlated in time only for short time intervals. We say that the lattice has a "short memory." Therefore no joint quasi-stationary state of a nuclear spin and the adjacent atoms has time to develop, but the lattice acts on the spin through rapidly and randomly fluctuating fields.

This situation is represented in the Liouville formulation as follows. A short memory of the lattice implies that the matrix elements of the Liouville interaction operator  $\mathbf{L}_1$ , connecting different eigenvectors of  $\mathbf{L}_b$ , vary very little over a large range of the corresponding eigenvalues  $\omega_{ab}$  of  $\mathbf{L}_b$ . Therefore, in the construction of matrix products involving  $(\omega - \mathbf{L}_0)^{-1}$  in Eqs. (34, 35, 54, or 55), the sum extends effectively over a broad range of eigenvalues of  $\mathbf{L}_0 = \mathbf{L}_s + \mathbf{L}_b$ . It follows that the effective, i.e., suitably averaged, value of  $\omega - \mathbf{L}_0$  in the matrix product is large and that the dimensionless products  $\mathbf{L}_1(\omega - \mathbf{L}_0)^{-1}$  or  $(\omega - \mathbf{L}_0)^{-1}\mathbf{L}_1$  are much smaller than 1 when the memory is sufficiently short.

Accordingly, the short-memory expansion *coincides with the perturbation expansion* on the right-hand side of (34) or (54). Because the reservoir has a continuous spectrum, it is not relevant or possible to gauge whether the interaction  $\mathbf{L}_1 = V - V^*$  is weak or strong in relation to the separation of energy levels as one does for discrete spectra or, equivalently, in (57). The relevant effective value of the resonance denominator is now seen to be determined not by the spectral intervals but by the speed of propagation of the interaction effect through the reservoir. One may say that the interaction effects remain weak because they accumulate coherently only over a single short memory period,  $\tau = [(\omega - \mathbf{L}_0)^{-1}]_{\text{eff}}$ .

Under conditions of short memory it is, therefore, appropriate to utilize the perturbation expansion (54) of  $\langle \mathbf{M}_c(\omega) \rangle$  and to break it off after its first significant term. The first term of the expansion,  $\langle \mathbf{L}_1 \rangle$  represents merely the effect of the average potential,  $\langle V \rangle$ , exerted by the reservoir on the system of interest. This term may be combined with  $\mathbf{L}_s$ . The next term  $\langle \mathbf{L}_1(\omega - \mathbf{L}_0)^{-1} \mathbf{L}_1 \rangle$  is the characteristic term of the short-memory approximation. Accordingly, this approximation

consists, to lowest order, of the assumption

$$\langle \mathbf{M}_c(\omega) \rangle \sim \langle \mathbf{L}_1 \rangle + \langle \mathbf{L}_1 \frac{1}{\omega - \mathbf{L}_0} \mathbf{L}_1 \rangle. \quad (59)$$

The main equation of the theory of nuclear spin relaxation (9) is equivalent to (59). Notice that, when (59) is substituted in (52) and the inverse transform (23) is calculated, relaxation is seen to proceed in the course of time as a function of the combination of variables  $\langle \mathbf{L}_1(\omega - \mathbf{L}_0)^{-1} \mathbf{L}_1 \rangle t$ . This combination is quadratic in the interaction energy and linear in the time and thus coincides with the combination which has been emphasized by Van Hove (10) and called by him " $\lambda^2 t$ ." More specifically we see here that the complete dimensional structure of the relevant combination of variables is  $(\mathbf{L}_1)^2 \tau t$ , where  $\tau$  is the memory period.

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# The Mathematics of Second Quantization for Systems of Fermions

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## I. Introduction<sup>1</sup>

It is the practice in most textbooks in which the subject of second quantization of many-fermion systems is discussed to give “plausibility” arguments only for the equivalence of configuration-space and second-quantized formalisms. This is undoubtedly because the actual proofs, as first constructed by Jordan (1) and Jordan and Wigner (2), are rather too lengthy and intricate to repeat in detail.

In a previous International Spring School of the University of Naples this subject was discussed by J. G. Valatin (3) in a lecture entitled “Second Quantization and Configuration Space Method.” In this lecture Valatin presented a treatment, which he had published some years earlier (4), that was much improved over that of Jordan and Wigner. Valatin’s improvement was in laying stress on the exact mathematical nature of the equivalence, in which the operations of annihilation and creation and the second-quantized description of states arise naturally as operations and elements of a long-known algebra of Grassman.

In one essential sense, however, the work of Valatin is still as complicated to repeat as that of Jordan and Wigner. This is because the equivalences in both cases are established by detailed comparisons of the complete sets of matrix elements of the one- and two-particle operators in configuration space and second-quantized formalisms. This is still

<sup>1</sup> The content of these notes is essentially the same as that of a paper by this author in *Proc. Phys. Soc.* **81**, 427 (1963).

sufficiently tedious, in spite of the basic elegance of Valatin's work, to seem to dissuade its widespread adoption as introductory material.

It has seemed to me that such complication is out of proportion to the simplicity of the results required, and in particular that it should not be necessary to treat separately the one-particle and two-particle operators, but that the general result for an operator  $\mathcal{O}$  depending symmetrically on the coordinates of  $f$  particles

$$\mathcal{O}^{(f)}(x^{s_1} \dots x^{s_f}) = \frac{1}{f!} \sum_{\substack{s_1 \dots s_f = 1 \\ s_1 \neq s_2 \neq \dots \neq s_f}}^N O(x^{s_1} \dots x^{s_f}), \quad (1)$$

should be derivable in a direct manner:

$$\mathcal{O}^{(f)} \equiv \frac{1}{f!} \sum_{\substack{s_1 \dots s_f \\ t_1 \dots t_f}} \langle t_1 \dots t_f | O | s_1 \dots s_f \rangle \alpha_{t_1}^+ \dots \alpha_{t_f}^+ \alpha_{s_f}^- \dots \alpha_{s_1}^-. \quad (2)$$

With the aid of a slightly different approach it is indeed possible to avoid the comparison of separate  $N$ -particle matrix elements, and Eq. (2) may be written down almost at sight (with some knowledge, of course, of exactly what is meant by second quantization) from an appropriate relation in configuration space. This relation [Eq. (7)] requires little effort to derive, but gives a new starting point for the second quantization of many-fermion systems that makes the comparison of the two formalisms almost trivially simple.

## II. The Operation in Configuration Space

A complete specification of the operator  $\mathcal{O}^{(f)}$  of Eq. (2) in the configuration space of an  $N$ -particle system can be given by either listing its matrix elements between a given set of basis wave functions in this space or, what can be almost the same thing, by writing down the result of the operation when performed on an arbitrary basis function. The latter specification is the one that we shall use; it does not necessarily require explicit calculation of the  $N$ -particle matrix elements, but can be written instead directly in terms of matrix elements between products of  $f$  single-particle wave functions.

The Hilbert space of  $N$ -fermion wave functions is built up from the space  $\mathfrak{R}$  of single-particle wave functions  $\psi_r$  by antisymmetrizing the tensor product of  $N$  identical spaces. This space has several notations in the literature, for instance,  $P_{s_n} \mathfrak{R} \otimes \mathfrak{R} \otimes \dots \otimes \mathfrak{R} = P_{s_n} \mathfrak{R}^{(N)}$  by Cook (5, 6) and  $A\mathfrak{R}^{\otimes N}$  by Kastler (7, 8); its covariant space is denoted as  $\wedge^N \mathfrak{R}$  by Valatin. We use Kastler's notation. A complete set of basis functions in this space is provided by the Slater determinants

$$\begin{aligned} \varphi_{r_1 \dots r_N}(x^1 \dots x^N) &= \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{r_1}(x^1) & \dots & \psi_{r_N}(x^1) \\ \dots & \dots & \dots \\ \psi_{r_1}(x^N) & \dots & \psi_{r_N}(x^N) \end{vmatrix} \\ &= \frac{1}{\sqrt{N!}} \sum_{\substack{\text{Perm} \\ x^1 \dots x^N}} \varepsilon^{x^1 \dots x^N} \psi_{r_1}(x^1) \dots \psi_{r_N}(x^N). \end{aligned} \quad (3)$$

In Eq. (3) the determinant is written out using the Levi-Civita densities  $\varepsilon^{x_1 \dots x_N}$  which take the values —1, 0, or +1 according as  $x^1 \dots x^N$  is ... odd, no, or an even permutation of the original order, respectively.

We operate with  $\mathcal{O}^{(f)}(x^{s_1} \dots x^{s_f})$  on an arbitrary Slater basis function of  $A\mathfrak{R}^{\otimes N}$ :

$$\mathcal{O}^{(f)} \varphi_{r_1 \dots r_N} = \frac{1}{f!} \sum_{\substack{s_1 \dots s_f=1 \\ s_1 \neq s_2 \neq \dots \neq s_f}}^N O(x^{s_1} \dots x^{s_f}) \frac{1}{\sqrt{N!}} \sum_{\substack{\text{Perm} \\ x^1 \dots x^N}} \varepsilon^{x^1 \dots x^N} \psi_{r_1}(x^1) \dots \psi_{r_N}(x^N). \quad (4)$$

Now  $O(x^{s_1} \dots x^{s_f}) \psi_{r_{s_1}}(x^{s_1}) \dots \psi_{r_{s_f}}(x^{s_f})$  is some function of  $x^{s_1} \dots x^{s_f}$  with the same boundary conditions as the  $\psi_r$ 's and can, therefore, be expanded in the set of functions  $\psi_{t_1}(x^{s_1}) \psi_{t_2}(x^{s_2}) \dots \psi_{t_f}(x^{s_f})$ , which form a complete basis set for such functions:

$$\begin{aligned} &O(x^{s_1} \dots x^{s_f}) \psi_{r_{s_1}}(x^{s_1}) \dots \psi_{r_{s_f}}(x^{s_f}) \\ &= \sum_{t_1 \dots t_f} F(t_1 \dots t_f, r_{s_1} \dots r_{s_f}) \psi_{t_1}(x^{s_1}) \dots \psi_{t_f}(x^{s_f}). \end{aligned} \quad (5)$$

Multiplication from the right by  $\psi_{t_1}^*(x^{s_1}) \dots \psi_{t_f}^*(x^{s_f})$  and integration over all  $x^{s_1} \dots x^{s_f}$  gives

$$\begin{aligned} F(t_1 \dots t_f, r_{s_1} \dots r_{s_f}) &= \int \dots \int \psi_{t_1}^*(x^{s_1}) \dots \psi_{t_f}^*(x^{s_f}) O(x^{s_1} \dots x^{s_f}) \\ &\quad \psi_{r_{s_1}}(x^{s_1}) \dots \psi_{r_{s_f}}(x^{s_f}) dx^{s_1} \dots dx^{s_f} \\ &= \langle t_1 \dots t_f | O | r_{s_1} \dots r_{s_f} \rangle. \end{aligned} \quad (6)$$

Using this expression in Eq. (4) and the fact that  $O$  is invariant under permutations of the  $x$ 's we obtain:

$$\begin{aligned}\mathcal{O}^{(f)} \varphi_{r_1 \dots r_N} &= \frac{1}{f!} \sum_{\substack{s_1 \dots s_f = 1 \\ s_1 \neq s_2 \neq \dots \neq s_f}}^N \frac{1}{\sqrt{N!}} \sum_{\text{Perm}} \varepsilon^{x_1 \dots x_N} \sum_{t_1 \dots t_f} \langle t_1 \dots t_f | O | r_{s_1} \dots r_{s_f} \rangle \\ &\times \psi_{r_1}(x^1) \dots \psi_{t_1}(x^{s_1}) \dots \psi_{t_f}(x^{s_f}) \dots \psi_{r_N}(x^N) \\ &= \frac{1}{f!} \sum_{\substack{s_1 \dots s_f = 1 \\ s_1 \neq s_2 \neq \dots \neq s_f}}^N \sum_{t_1 \dots t_f} \langle t_1 \dots t_f | O | r_{s_1} \dots r_{s_f} \rangle \varphi_{r_1 \dots t_1 \dots t_f \dots r_N}.\end{aligned}\quad (7)$$

Equation (7) gives a complete specification of the operator. The matrix elements of  $\mathcal{O}$  between any pair of basis functions in  $A\mathfrak{R}^{\otimes N}$  could be calculated, if required, from this equation. Tabulation of these is, in general, exceedingly complicated and Eq. (7) probably represents the most concise way of summarizing these properties. When  $f = N$  we have the particular case:

$$\mathcal{O}^{(N)}(x^1 \dots x^N) = \frac{1}{N!} \sum_{\substack{\text{Perm} \\ x^1 \dots x^N}} O(x^1 \dots x^N) = O(x^1 \dots x^N). \quad (8)$$

In this case Eq. (7) reduces to:

$$\mathcal{O}^{(N)} \varphi_{r_1 \dots r_N} = \sum_{s_1 \dots s_N} \langle s_1 \dots s_N | O | r_1 \dots r_N \rangle \varphi_{s_1 \dots s_N} \quad (9)$$

which can be shown by a straightforward calculation to be equal to

$$\mathcal{O}^{(N)} \varphi_{r_1 \dots r_N} = \sum_{s_1 \dots s_N} \langle \varphi_{s_1 \dots s_N} | \mathcal{O} | \varphi_{r_1 \dots r_N} \rangle \varphi_{s_1 \dots s_N} \quad (10)$$

which is the usual representation.

### III. The Operation in Second Quantization

The isomorphism between the elements  $e$  of the Grassmann space algebra<sup>2</sup>  $\mathcal{G}(\mathfrak{R})$  on  $\mathfrak{R}$  (generated by taking the outer products 1, 2, 3, ...

<sup>2</sup> Sufficient knowledge of this algebra to understand second quantization can be obtained from the book by Littlewood (9).

at a time of a set of primitive elements  $a_r$ , isomorphic with  $\psi_r$ ), and the Slater basis functions of the complete fermion state space,

$$\bigotimes_{N=0}^{\infty} A\mathfrak{R}^{\otimes N},$$

[Fock (10)] has been demonstrated by Valatin. The outer product of two ordered elements  $e_i, e_j$ , is defined by the rule

$$e_i e_j = -e_j e_i. \quad (11)$$

In this isomorphism the Slater wave function  $\varphi_{r_1 \dots r_N}(x^1 \dots x^N)$  corresponds 1 : 1 with the algebraic element  $e_r^N = a_{r_1} a_{r_2} \dots a_{r_N}$ . This is the “occupation number representation” of second quantization. The outer product by a primitive element  $a_r$  is denoted by  $a_r^\dagger |$  and is the familiar creation operation for Fermi particles. The inner product by  $a_r$ , denoted  $a_r |$  or  $(a_r, |$  is the annihilation operation. Interior multiplication of two ordered normalized elements  $e_i, e_j$ , is defined as follows. Given an element  $e_j$  such that  $e_i$  is a left factor, that is, there exists an element  $e_k$  such that

$$e_j = e_i e_k, \quad (12)$$

then the inner product is defined by

$$(e_i, e_j) = (e_i, e_i e_k) = (e_i, e_i) e_k = e_k \quad (13a)$$

if  $e_i$  is not a left factor of  $e_j$  then

$$(e_i, e_j) = 0. \quad (13b)$$

This operation is the exact inverse of exterior multiplication.

Second quantization of Eq. (7) consists simply of rewriting it in its corresponding algebraic form. It thus becomes

$$e_r^N = \frac{1}{f!} \sum_{\substack{s_1 \dots s_f = 1 \\ s_1 \neq s_2 \dots \neq s_f}} \sum_{t_1 \dots t_f} \langle t_1 \dots t_f | O | r_{s_1} \dots r_{s_f} \rangle a_{r_1} \dots a_{t_1} \dots a_{t_f} \dots a_{r_N}. \quad (14)$$

By use of the multiplication rules (11) and (13) of the algebra, which are the familiar rules for using the creation and annihilation operators for

Fermi particles, Eq. (14) can be written in the alternative form:

$$e_r^N = \frac{1}{f!} \sum_{\substack{s_1 \dots s_f = 1 \\ s_1 \neq s_2 \dots \neq s_f}}^N \sum_{t_1 \dots t_f} \langle t_1 \dots t_f | O | r_{s_1} \dots r_{s_f} \rangle \alpha_{t_1}^\dagger \alpha_{t_2}^\dagger \dots \alpha_{t_f}^\dagger \alpha_{r_{s_1}} \dots \alpha_{r_{s_f}} \alpha_{r_{s_1}} | e_r^N \quad (15)$$

The restrictions on the first sum may be removed since it may be seen by use of (11) and (13) that the additional terms are all zero. By a slight change of suffies Eq. (15) gives the final form of the operator as predicted in Eq. (2).

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# Correlation Functions and Macroscopic Equations

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In recent years there has been widespread discussion of the possibility of using time-dependent correlation functions to conveniently and exactly describe the behavior of a system disturbed slightly from a steady state. For a considerably longer time, it has been recognized that macroscopic equations exactly describe a system departing slowly in space and time from a steady state. Examples of such macroscopic equations are the Maxwell equations for electromagnetic phenomenon in media and the Navier-Stokes hydrodynamic equations of a one-component fluid. There are consequently *two exact* formulations that determine the behavior of systems which are *both slightly and slowly* disturbed from equilibrium. The first of these is the macroscopic or hydrodynamic description, which can be taken in a linearized form because of the restriction to weak disturbances. The second is the description in terms of the long wavelength, low frequency correlation functions. We would like to discuss in this chapter how the phenomena predicted by both descriptions make their appearance in the correlation function description. Thus, we will be concerned primarily with what macroscopic physics tells us about the correlation functions and only in a very peripheral way with what the correlation functions teach us about macroscopic physics.<sup>1</sup>

As we shall see, the hydrodynamical description implies considerable structure for the correlation function — structure which is not immediately apparent nor simply derivable from perturbative calculations of the time-dependent correlation functions. This is hardly surprising since hydrodynamics is relevant to the discussion of disturbances in which a

<sup>1</sup> Most of the material contained in these lectures is contained in an article by L. P. Kadanoff and P. C. Martin, *Ann. Phys. (N.Y.)*, 24, 419–469 (1963).

local equilibrium is continually enforced, whereas perturbation techniques, at least in their more primitive forms, pertain to the discussion of short-time effects in terms of successive collisions.

This difficulty does not preclude the deduction of the macroscopic description from the microscopic description by perturbation theory. It is merely an indication that this deduction is not a trivial matter, because it requires a discussion of long time, large distance behavior of the correlations. Indeed, such analysis has been carried out in certain special cases. Performing it more generally is closely analogous to (but more complicated than) renormalizing quantum field theory. Indeed, the transport coefficients and thermodynamic derivatives play a similar role to the renormalized masses and coupling constants of elementary particle physics. The best perturbation techniques seek to determine these quantities self-consistently from equations involving residual interactions between the nearly independent renormalized modes resulting from the repeated effects of the interparticle forces.

If we could carry out from first principles, the inverse of the procedure we shall discuss, the computation of the correlation functions in stationary states in terms of the time-independent forces applied at their boundaries and their interparticle forces, we would have far more information than the macroscopic equations provide. First, we would have information about the effect of disturbances which are slight but have *high frequency and wave number*. Secondly, we would determine the *values* of the *dissipative coefficients* which occur as parameters in the hydrodynamic equations, and of the *thermodynamic derivatives* in the equation of state which supplement these equations. Thirdly, we would be able to ascertain what macroscopic equations were appropriate for a given system. After all, not every one-component system satisfies the same macroscopic equations nor requires the same number of thermodynamic and macroscopic parameters. In addition to ordinary fluids there are turbulent fluids (with velocity correlations), superfluids (with two velocities and densities), and solids (with a shear modulus as well as a bulk modulus, and with directionally dependent transport coefficients).

Actually, this third advantage, the ability to determine from first principles what parameters are required for a given interacting system, is rather illusory. All that may truly be determined deductively is whether

an assumed kinetic description is tenable for the system. That is to say, we could deduce whether a steady state with certain assumed symmetry properties was stable, or whether, by contrast, spontaneous fluctuations in a system having these symmetry properties tended to grow. For example, if we sought a stationary solution for a system with a density matrix that had the symmetry properties appropriate to a fluid, we would obtain by correlation function techniques the hydrodynamical equations appropriate to a fluid. We would also discover an instability in the correlation functions for the liquid in the region in which the supercooled liquid was unstable. We would not, however, have even a hint of the solid in the supercooled region in which, for the given temperature and pressure, the solid was more likely than the assumed fluid configuration, but the fluid configuration was also stable to microscopic perturbations. To determine the elastic constants of a solid with a particular symmetry, it is necessary to investigate solutions in which the correlation functions have that symmetry.

The point of this diatribe is to stress that the correlation function procedures developed thus far are also not entirely deductive. They too require a separate investigation of the properties which constitute a specified steady state. In the correlation function description this amounts to the classification of possible solutions of the nonlinear integro-differential equations for the exact correlation functions. This classification of the symmetry properties of different steady-state solutions proceeds along the same lines as does the classification of the possible macroscopic equations that can describe many particle systems. The real advantages of the correlation function techniques, then, are (i) the *ability to compute desired macroscopic parameters for systems with given symmetries from microscopic parameters*, and (ii) *the ability to determine information relating to the kinetic stage* — information that not only determines the parameters of the hydrodynamic stage, but characterizes the results of other experiments like neutron scattering and ultrasonic response, which involve high frequency and wave number probes. We shall not discuss either of these aspects extensively in what follows, since they have been extensively discussed in other chapters and in the literature.

## I. Illustrative Example

In order to understand the kind of information contained in the macroscopic equations and how it appears in the long-wavelength, low-frequency form of the correlation function, let us turn directly to a simple model in which the macroscopic description is characterized by a single conservation law and phenomenological equation, and in which the associated equation of state consists of a single thermodynamic derivative. We consider spin diffusion in a liquid with no spin-dependent forces (or equivalently the diffusion of isotopes with chemically identical properties). That is to say, we consider diffusion of spin in a system in which the spin serves as a label and has no dynamical significance.

### A. MACROSCOPIC DESCRIPTION

We denote by  $M(\mathbf{r}, t)$  the magnetization at the point at time  $t$ . The magnetization, proportional to the net imbalance of spin, is given by

$$M(\mathbf{r}, t) = \sum_{\nu} \gamma s_{\nu}(t) \delta(\mathbf{r} - \mathbf{r}_{\nu}(t)),$$

where  $\gamma$  is the gyromagnetic ratio and  $s_{\nu}$  the spin density. The magnitude of  $s_{\nu}$  will be taken as  $\frac{1}{2}$  thus particularizing the notation to a physical problem of experimental interest, spin diffusion in liquid He<sup>3</sup>. The three statements which constitute the macroscopic description are:

- (1) A conservation law for the total spin

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

where

$$\mathbf{j}^M(\mathbf{r}, t) = \sum_{\nu} \gamma s_{\nu}(t) \{ \mathbf{p}_{\nu}(t), \delta(\mathbf{r} - \mathbf{r}_{\nu}(t)/2m) \}. \quad (1)$$

- (2) A phenomenological transport equation saying spin imbalances will diffuse

$$\langle \mathbf{j}^M(\mathbf{r}, t) \rangle = -D \nabla \langle M(\mathbf{r}, t) \rangle. \quad (2)$$

The quantity  $D$ , the diffusion constant, is positive.

(3) An equation of state relating the field and magnetization

$$\chi = \frac{\partial M}{\partial H} \Big|_{H=0} \quad (3)$$

We may employ these three statements to solve the problem in which we adiabatically apply a magnetic field  $H(\mathbf{r})$  varying slowly in space for  $t < 0$  and turn it off at  $t = 0$ . From the first two equations we have

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

Introducing the Fourier-Laplace transforms

$$\begin{aligned} M(\mathbf{k}, z) &= \int d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} \int_0^\infty dt e^{izt} \langle M(\mathbf{r}, t) \rangle, \\ H(\mathbf{k}) &= \int d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} H(\mathbf{r}), \end{aligned} \quad (4)$$

we write the equation which determines the behavior of the magnetization for  $t > 0$  in the form

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

We then use property (3) to deduce that for long wavelength disturbances

$$M(\mathbf{k}, z) = \frac{\chi H(\mathbf{k})}{-iz + Dk^2}. \quad (5)$$

## B. CORRELATION FUNCTION DESCRIPTION OF SIMPLE EXAMPLE

Let us now find a solution to the same problem using the correlation function description. In order to develop the correlation function description of spin diffusion, we notice that an external magnetic field can be represented by an extra time-dependent term added to the Hamiltonian of the system

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

According to standard techniques of quantum-mechanical perturba-

tion theory, the linear change in the average of any operator,  $A(\mathbf{r}, t)$ , induced by an extra term in the Hamiltonian is

$$\delta \langle A(\mathbf{r}, t) \rangle = -i \int_{-\infty}^t dt' [\langle A(\mathbf{r}, t), \delta \mathcal{H}(t') \rangle].$$

This equation applies to a system which was in a steady state before the disturbance was introduced; the expectation value of the right-hand side,  $\langle [A(\mathbf{r}, t), \delta \mathcal{H}(t')] \rangle$  is the expectation value in that steady state.

In our example we have

$$\begin{aligned} \langle M(\mathbf{r}, t) \rangle &= i \int_{-\infty}^t dt' e^{i\omega t'} \int d\mathbf{r}' H(\mathbf{r}') \langle [M(\mathbf{r}, t), M(\mathbf{r}', t')] \rangle, \quad t \leq 0, \\ &= i \int_{-\infty}^0 dt' e^{i\omega t'} \int d\mathbf{r}' H(\mathbf{r}') \langle [M(\mathbf{r}, t), M(\mathbf{r}', t')] \rangle, \quad t \geq 0. \end{aligned} \quad (6)$$

In order to compare (6) with the result of our hydrodynamic discussion, we introduce an integral representation for the commutator of the magnetization at different space-time points. Because of the space-time translational invariance of the equilibrium system we may write

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

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

The expression for  $\langle M(\mathbf{r}, t) \rangle$  now becomes

$$\begin{aligned} \langle M(\mathbf{r}, t) \rangle &= \int \frac{d\mathbf{k}}{(2\pi)^3} H(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{r}} \int \frac{d\omega}{\pi} \frac{\chi''(k, \omega)}{\omega} \quad \text{for } t \leq 0, \\ &= \int \frac{d\mathbf{k}}{(2\pi)^3} H(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{r}} \int \frac{d\omega}{\pi} \frac{\chi''(k, \omega)}{\omega} e^{-i\omega t} \quad \text{for } t \geq 0. \end{aligned} \quad (7)$$

From the first of these equations we may identify the function multiplying  $H(\mathbf{r})$  with  $\chi$ . From the second we may obtain an expression

for  $M(\mathbf{k}, z)$  by employing the same Laplace-Fourier transform, (4), introduced in the hydrodynamic description

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

The hydrodynamical description gave an expression for  $M(\mathbf{k}, z)$  appropriate in the limit of small  $\mathbf{k}$ . The above equation expresses this function in terms of  $\chi''(\mathbf{k}, \omega)$ . We can therefore use the two to solve for  $\chi''(\mathbf{k}, \omega)$  in the long wavelength limit. We shall assume that we are concerned with times short, and therefore frequency differences large compared to the the frequency spacings over which  $\chi''(\mathbf{k}, \omega)$  averages to a smooth function the frequency.<sup>2</sup>

We may then write

$$\lim_{\epsilon \rightarrow 0} \frac{1}{\omega' - \omega - i\epsilon} = \mathcal{P} \frac{1}{\omega' - \omega} + \pi i \delta(\omega - \omega') ,$$

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

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

Comparison with (4) yields the expression

$$\chi''(\mathbf{k}, \omega) = \frac{\chi D k^2 \omega}{\omega^2 + (Dk^2)^2} . \quad (8)$$

Of course, since the hydrodynamic equations are valid only for slowly varying disturbances, the identification is only correct for  $\chi''$  at small  $k$  and  $\omega$ .

### C. RIGOROUS FEATURES OF CORRELATION FUNCTION DESCRIPTION

The three properties we invoked in our hydrodynamical discussion each have a rigorous counterpart for the function  $\chi''(\mathbf{k}, \omega)$  or the related

<sup>2</sup> It is here that we mathematically introduce irreversibility since  $\chi''(\mathbf{k}, \omega)$  is really a distribution of  $\delta$ -functions and not a smooth function. This leads of course to almost periodic behavior on a time scale of no interest to us, since the frequency spacings are so ridiculously small for a large system.

function, the dynamic susceptibility  $\chi$  which is analytic except on the real axis

$$\chi(k, z) = \int \frac{d\omega'}{\pi} \frac{\chi''(k, \omega')}{\omega' - z}, \quad (9)$$

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

The first statement we incorporate in the discussion of  $\chi$  is the previously utilized property (3). In general, when slowly varying fields coupled to the conserved quantities are adiabatically applied to a system in a steady state, a new stationary state with altered values of the conserved quantities is induced. In the long-wavelength limit, the coupling fields are the conjugate thermodynamic variables, and the changes in the conserved quantities (which are expressed in terms of the matrix  $\chi$ ) may also be expressed by a matrix of thermodynamic derivatives determined by the equation of state. In our example, this matrix is the single coefficient which gives the conserved quantity  $M(\mathbf{k})$  in terms of  $H(\mathbf{k})$  the adiabatically applied field. Its incorporation in the discussion of  $\chi$  occurs through the statement that, as  $k \rightarrow 0$ ,  $\chi(k) \rightarrow dM/dH$ .

The property (2), or at least that part of its content ( $D > 0$ ) which is generally rigorous, is the statement that the phenomenological law must be dissipative in a stable system. The counterpart of this property, an aspect of the second law of thermodynamics, is the stability requirement for the correlation function matrix (in our example, a single function)

$$\omega\chi''(k, \omega) \geq 0. \quad (10)$$

In particular, it can be shown that  $\omega\chi''(k, \omega)$  is a measure of the work done by an external field in changing the system, and thus that  $\omega\chi''(k, \omega) \geq 0$  is a condition for stability. It can also be proven that this condition is automatically satisfied in a canonical ensemble which necessarily predicts stable correlation functions.

The property (1), the conservation law, permits us to write another sum rule, like (7). In particular it follows from the conservation law that

$$\mathbf{k} \cdot \int d\mathbf{r} e^{-i\mathbf{k} \cdot \mathbf{r}} [\mathbf{j}^M(\mathbf{r}, 0), M(0, 0)] = \int \frac{d\omega}{\pi} \omega\chi''(k, \omega). \quad (11)$$

Without evaluation, we may deduce that since the integrand on the

lef-hand side of (11) is a vector quantity, it will be proportional to  $k$  and consequently that the first moment of  $\chi''$  will be proportional to  $k^2$ . Because the left-hand side is essentially the commutator of momentum and position there is no difficulty in actually calculating it for our simple example, obtaining

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

Strictly speaking, the value of the coefficient of  $k^2$  is outside the realm of hydrodynamics. The proportionality to  $k^2$ , and thus the fact that  $\chi''(k, \omega)$  vanishes as  $k \rightarrow 0$  reflects property (1), the hydrodynamical content. In fact, the sum rule (11) is not really satisfied by the hydrodynamical description since the phenomenological laws predict a proportionality to  $k^2$  but with an infinite constant. This is not a very serious defect since the sum rule (11) weighs high frequencies while our hydrodynamic form for  $\chi''(k, \omega)$  is only correct at low frequencies.

The physical reason for this failure is easy to understand. We have stated in our phenomenological law that the short-time response is dissipative and thus overestimated the dissipation at high frequencies. In fact, the short-time behavior is reversible not dissipative; only the long-time behavior is dissipative. There is a natural way to take this property into account phenomenologically. We must change our equation from a first-order one, which has only resistance, to a second-order one, which exhibits an inductive behavior at high frequencies. We therefore write

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

For variations that occur over times long compared to  $\tau$ , the equation is identical to our hydrodynamic description. But for rapid variations in time, our modified equation leads to a predominantly nondissipative response. With the aid of this equation the hydrodynamical analysis we applied previously can be carried through once more. We find in particular

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

The high frequency sum rule can be satisfied with this phenomenological description. We need only require that the relaxation time satisfy

$$D = \frac{n\gamma^2}{4m} \frac{\tau}{\chi}. \quad (12)$$

That is to say, a minimal form for  $\chi''$  consistent with properties (1), (2), and (3) is the single collision time approximation

$$\begin{aligned} \chi''(k, \omega) &= \frac{\chi D k^2 \omega}{\omega^2 + D^2 [k^2 - (4\omega^2 \chi m / n\gamma^2)]^2}, \\ \chi(k, z) &= \chi + \frac{iM(k, z)z}{H(k)} = \chi \left(1 - \frac{iz}{Dk^2} - \frac{4z^2 \chi m}{n\gamma^2 k^2}\right)^{-1}, \\ \frac{1}{\chi(k, z)} - \frac{1}{\chi} &= -\frac{4mz^2}{n\gamma^2 k^2} - \frac{iz}{D\chi k^2}. \end{aligned} \quad (8')$$

While this phenomenological modification is not exact, certain general features of it, e.g.,  $D \rightarrow 0$  as  $\chi \rightarrow \infty$ , are experimentally verifiable. The condition for it to be approximately correct will now be made precise by incorporating the rigorous counterparts of our three basic properties to construct a dispersion integral representation of the correlation function. As we shall see, these counterparts lead to a representation of  $\chi$  which exhibits many facets of the hydrodynamic description (8'). It leads to (8') when a spectral function is assumed to be slowly varying. When this function is not slowly varying the system will be described by other slowly varying functions, and the hydrodynamics will differ.

From the stability condition,  $\omega\chi''(k, \omega) > 0$ , property (2), in the form (10), it can be shown that

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

has an imaginary part proportional to the imaginary part of  $\gamma$ . Therefore,  $\chi(k, z)$  is analytic except on the real axis. Furthermore, the conservation law, property (1), as employed in the moment sum rule (11), tells us that

$$\chi^{-1}(k, z) \xrightarrow[z \rightarrow \infty]{} -\frac{4z^2 m}{n k^2 \gamma^2}.$$

Finally, property (3), in the form of the thermodynamic sum rule (7), tells us that  $\chi^{-1}(k)$  exists and approaches the thermodynamic derivative as  $k \rightarrow 0$ . Putting these properties together we have that

$$\frac{nk^2\gamma^2}{4mz^2} [\chi^{-1}(k, z) - \chi^{-1}(k)] + 1$$

is analytic in  $z$ , vanishes as  $z \rightarrow \infty$ , and is finite for  $z \rightarrow 0$ .

We can therefore write

$$\frac{nk^2\gamma^2}{4mz^2} [\chi^{-1}(k, z) - \chi^{-1}(k)] + 1 = \frac{n\gamma^2}{4m\chi(k)} \int \frac{d\omega}{\pi} \frac{\alpha(k, \omega)}{z^2 - \omega^2}. \quad (13)$$

The regularity property which leads to the hydrodynamic description constructed phenomenologically results when  $\alpha$  is approximately constant for small values of  $k$  and  $\omega$ . In that case we may write, for small  $k$  and  $\omega$ ,

$$\frac{nk^2\gamma^2}{4mz^2} [\chi^{-1}(k, z) - \chi^{-1}(k)] + 1 \cong \frac{-in\gamma^2}{4m\chi(k)} \frac{\alpha(0, 0)}{z},$$

which is precisely the form (8') we determined phenomenologically when  $\alpha(0, 0) = 1/D$ . We cannot, of course, infer from general properties that  $\alpha$  is regular, nonvanishing, and slowly varying — the part of property (2) that depends on the microscopic details of the system. All we can say is that if this were not the case the hydrodynamical equations would be different. For example, in an ordinary fluid, identical arguments lead to an identical dispersion relation for the density correlation function. However the corresponding function,  $\alpha$ , behaves as  $k^2$  for small  $\omega$ , reflecting the fact that the time derivative of the density (the momentum) is also conserved. Also, at appreciable temperatures,  $\alpha$  contains a significant term, which is not regular but depends on the ratio of  $k$  and  $\omega$ . In consequence, the low-temperature microscopic description involves sound waves instead of diffusion, and the high-temperature description involves coupled sound waves and heat diffusion.

#### D. CONSEQUENCE OF DETAILED BALANCE FOR THE SIMPLE EXAMPLE

Before discussing the ordinarily fluid, let us point out some additional properties satisfied by the  $\chi$  of our simple example because it is expressed

as a steady-state correlation function. These relations follow because there is in a steady state a connection between  $\chi''$ , the commutator that characterizes dissipation, and the anticommutator that describes fluctuations. This connection expresses a relationship in transition rates between substates of different energy in a macroscopic steady state — a condition of detailed balance. Specifically the detailed balance condition requires that the ratio of transition probabilities between substates having different values of the parameters characterizing conserved variables must equal the ratio of the density of substates with these parameters.

For the particular case in which the steady state is an equilibrium state characterized by a canonical ensemble, the ratio of densities of the substates with energies  $E_1$  and  $E_2$  is  $e^{\beta\omega}$ , where  $\omega$  is the difference in energy between the two substates and  $\beta = 1/kT$  is the inverse temperature. In that case, the detailed balance condition is easily stated and proven. Moreover, in that case, we may express the detailed balance condition by the equivalent and familiar fluctuation-dissipation theorem. The difference in transition probabilities between substates (which is equal to the dissipation per unit intensity of external field divided by the energy) is  $\chi''(k, \omega)$ . It is related to the sum of transition probabilities, the Fourier transform of the fluctuations, by

$$\begin{aligned} \frac{1}{2} \text{ sum} &= \frac{1}{2} \left( \frac{e^{\beta\omega} + 1}{e^{\beta\omega} - 1} \right) (\text{diff}) = \frac{1}{2} \left( \coth \frac{\beta\omega}{2} \right) \chi''(k, \omega) \\ &= \left[ \frac{1}{2} + \frac{1}{e^{\beta\omega} - 1} \right] \chi''(k, \omega). \end{aligned}$$

Thus we may write, for equilibrium expectation values,

$$\begin{aligned} &\langle \{A_i(\mathbf{r}, t) - \langle A_i \rangle_{\text{eq}}, A_j(\mathbf{r}', t') - \langle A_j \rangle_{\text{eq}}\} \rangle \\ &= \int \frac{d\omega}{\pi} \int \frac{d\mathbf{k}}{(2\pi)^3} e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')-i\omega(t-t')} \coth \frac{\beta\omega}{2} \chi''_{ij}(\mathbf{k}, \omega), \end{aligned} \quad (14)$$

a statement that may be easily and directly verified by formal manipulations.

It follows from the fluctuation-dissipation theorem that the static

magnetic form factor  $S(\mathbf{k})$  is given by

$$\begin{aligned} S(\mathbf{k}) &\equiv \int d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} \langle \frac{1}{2} \{M(\mathbf{r}, 0), M(0, 0)\} \rangle \\ &= \int \frac{d\omega}{2\pi} \left[ \frac{1}{2} + \frac{1}{e^{\beta\omega} - 1} \right] \chi''(k, \omega). \end{aligned} \quad (15)$$

It also follows that the relation we have derived,

$$D\chi = \lim_{\omega \rightarrow 0} \left[ \lim_{k \rightarrow 0} \frac{\omega}{k^2} \chi''(k, \omega) \right], \quad (16)$$

can be expressed in terms of the magnetization anticommutator as

$$D\chi = \lim_{\omega \rightarrow 0} \left[ \lim_{k \rightarrow 0} \int d\mathbf{r} \int dt e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}') + i\omega(t-t')} \frac{\omega^2}{k^2} \frac{\beta}{4} \langle \{M(\mathbf{r}, t), M(\mathbf{r}', t')\} \rangle_{eq} \right] \quad (17)$$

or

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

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

In other steady states which cannot be described by canonical or grand canonical ensembles the additional relations resulting from the requirement of detailed balance, when known, are more complicated. In some simple cases like ferromagnets or superfluids there is no change. Others are treated by several chemical potentials or by means of frequency-dependent temperatures.

## II. Application to One-Component Fluids

### A. HYDRODYNAMIC DESCRIPTION

In the remainder of this chapter we will indicate how the kind of analysis illustrated above applies to more complicated systems. In particular, we will discuss fully the parallel of the previous discussion for a

normal one-component fluid and indicate some important modifications that arise for a superfluid at various points in the discussion.

For a one-component fluid, there is a conservation law and transport equation for the density of particles  $n(\mathbf{r}, t)$ , the momentum density  $\mathbf{g}(\mathbf{r}, t)$ , and the energy density  $\varepsilon(\mathbf{r}, t)$ . These conservations laws can be written as

$$\frac{\partial}{\partial t} n(\mathbf{r}, t) + \nabla \cdot \mathbf{g} \frac{(\mathbf{r}, t)}{m} = 0 \quad \text{number conservation,} \quad (18a)$$

$$\frac{\partial}{\partial t} \mathbf{g}(\mathbf{r}, t) + \nabla \cdot \tau(\mathbf{r}, t) = 0 \quad \text{momentum conservation,} \quad (18b)$$

$$\frac{\partial}{\partial t} \varepsilon(\mathbf{r}, t) + \nabla \cdot \mathbf{j}^e(\mathbf{r}, t) = 0 \quad \text{energy conservation.} \quad (18c)$$

Here,  $\mathbf{j}^e$  is the energy current density and  $\tau$  is the stress tensor, which serves as a momentum current.

Again these equations must be supplemented in two ways. First, we must suppose that, when all variations in space and time are slow, the system can be treated as if it were in thermodynamic equilibrium locally. Since the state of the fluid in equilibrium is characterized by the five conserved variables or five associated intensive variables, we expect local equilibrium to be characterized either by the local densities of the conserved variables or by related spatially and temporally varying intensive quantities. Conventionally these are chosen to be the temperature, pressure, and average velocity.

In a superfluid, the five conserved variables do not completely specify the system. There are, in addition, order parameters associated with the superfluid velocity,  $v_s$  and its density variation. In this case the macroscopic equations also include equation of motion for the order parameter and phenomenological law for the "forces"<sup>3</sup> which occur in them. These phenomenological laws involve gradients of both the conserved quantities and the order parameters.

<sup>3</sup> The forces are the quantities which vanish in the long wavelength limit and are equal to the time rate of change of the order parameters, e.g., in a superfluid the force is given by  $\partial v_s / \partial t = -\nabla \mu$ .

We define an average velocity by writing the momentum density as

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

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

$$\langle \mathbf{g}(\mathbf{r}, t) \rangle = nm \mathbf{v}(\mathbf{r}, t), \quad (19a)$$

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

$$\mathbf{j}^e = (\varepsilon + p)\mathbf{v}.$$

If the system is in local mechanical equilibrium and if there are no order parameters or the order parameters are unchanged by a Galilean transformation the mechanical contribution to the local energy current must also have this form. However, if there is a temperature gradient in the local equilibrium system there will be an additional dissipative flow of energy from hot regions to cold regions. As a result the energy current in local equilibrium takes the form

$$\mathbf{j}^e(\mathbf{r}, t) = (\varepsilon + p) \mathbf{v}(\mathbf{r}, t) - \kappa \nabla T(\mathbf{r}, t), \quad (19c)$$

where  $\varepsilon$  and  $p$  are the equilibrium parameters. The coefficient  $\kappa$  is called the thermal conductivity. The temperature is of course not an independent variable but connected with the others by the usual thermodynamic relations. Thus, a change in the temperature is related to changes in the density and energy density by

$$\nabla T(\mathbf{r}, t) = \frac{\partial T}{\partial n} \Big|_{\varepsilon} \nabla n(\mathbf{r}, t) + \frac{\partial T}{\partial \varepsilon} \Big|_n \nabla \varepsilon(\mathbf{r}, t).$$

In the non rotating superfluid there is an additional order parameter, the superfluid velocity, which is altered, under Galilean transformation. Furthermore, there can be a dissipationless flow of energy and matter

in the frame in which the velocity vanishes. Consequently, neglecting dissipative terms, we have

$$\mathbf{j}^e(\mathbf{r}, t) = (\varepsilon + p) \mathbf{v}(\mathbf{r}, t) + \frac{TS}{mN} \varrho_s [\mathbf{v}_n(\mathbf{r}, t) - \mathbf{v}_s(\mathbf{r}, t)], \quad (19c')$$

where  $(S/mN)$  is the entropy per unit mass. This equation serves to define  $\varrho_s$ , the density of superfluid in terms of the order parameter,  $\mathbf{v}_s$ , and  $\mathbf{v}_n$  defined by  $\mathbf{g} = \varrho_s \mathbf{v}_s + (\varrho - \varrho_s) \mathbf{v}_n$ .

To complete the set of equations, it is necessary to specify the stress tensor  $\tau_{ij}$ . For a fluid at rest in complete equilibrium the stress tensor takes the form

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

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

$$\tau_{ij}(\mathbf{r}, t) = \delta_{ij} p(\mathbf{r}, t) - \eta \left( \frac{\partial \mathbf{v}_i(\mathbf{r}, t)}{\partial r_j} + \frac{\partial \mathbf{v}_j(\mathbf{r}, t)}{\partial r_i} \right) - \delta_{ij} \nabla \cdot \mathbf{v}(\mathbf{r}, t) \left( \zeta - \frac{2}{3} \eta \right). \quad (19b)$$

Here  $\eta$  is called the viscosity and  $\zeta$  the second viscosity or bulk viscosity. In a superfluid there will be additional terms arising from the dissipative effects dependent on the gradients of  $\mathbf{v}_s$  and also, if it is rotating and there are vortices, nondissipative terms depending on the local vorticity. Changes in the pressure are also related to changes in the energy and density through thermodynamic relations.

Finally the "force" associated with  $\mathbf{v}_s$  is expressed as a change in the chemical potential (and therefore in the energy and density) along with a dissipative contribution involving additional viscosities. Here also, an additional nondissipative term, a Magnus force, is present when there are vortices.

We may recombine the normal fluid equations in a form which is convenient for our purposes. With the aid of the momentum conservation law we obtain

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

Therefore the transverse part of the momentum satisfies the diffusion equation

$$\frac{\partial}{\partial t} \langle \mathbf{g}_t(\mathbf{r}, t) \rangle = \frac{\eta}{mn} \nabla^2 \langle \mathbf{g}_t(\mathbf{r}, t) \rangle. \quad (20)$$

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

$$\left[ -m \frac{\partial^2}{\partial t^2} + \frac{\frac{4}{3}\eta + \zeta}{n} \frac{\partial}{\partial t} \nabla^2 \right] \langle n(\mathbf{r}, t) \rangle + \nabla^2 p(\mathbf{r}, t) = 0. \quad (21)$$

For a normal fluid we have

$$\frac{\partial}{\partial t} \left[ \varepsilon \langle \mathbf{r}, t \rangle - \frac{\varepsilon + p}{n} \langle n(\mathbf{r}, t) \rangle \right] - \lambda \nabla^2 T(\mathbf{r}, t) = 0. \quad (22)$$

For a superfluid, neglecting all dissipative terms and effects of vorticity, and eliminating  $\mathbf{v}_s$  with the aid of  $\dot{\mathbf{v}}_s = -\nabla \mu$ , we obtain

$$\frac{\partial^2}{\partial t^2} \left[ \langle \varepsilon(\mathbf{r}, t) \rangle - \frac{\varepsilon + p}{n} \langle n(\mathbf{r}, t) \rangle \right] - \frac{TS^2 \varrho_s}{N^2 m \varrho_n} \nabla^2 T(\mathbf{r}, t) = 0, \quad (22')$$

where

$$\varrho = \varrho_s + \varrho_n.$$

Equations (22) and (22') for normal fluids and superfluids become identical when  $\varrho_s$  is set equal to zero and dissipation is neglected.

The analysis of the equation for the transverse momentum follows along exactly the same lines as the analysis of spin diffusion given earlier. The equations for  $\varepsilon$  and  $n$  are analyzed in a very similar way. We define

$$\begin{aligned} n(\mathbf{k}, z) &= \int d\mathbf{r} \int_0^\infty dt e^{-i\mathbf{k}\cdot\mathbf{r}+izt} \langle n(\mathbf{r}, t) \rangle, \\ p(\mathbf{k}, z) &= \int d\mathbf{r} \int_0^\infty dt e^{-i\mathbf{k}\cdot\mathbf{r}+izt} p(\mathbf{r}, t), \\ n(k) &= \int d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} \langle n(\mathbf{r}, 0) \rangle, \\ p(k) &= \int d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} \langle p(\mathbf{r}, 0) \rangle. \end{aligned}$$

We also notice that we can guarantee that  $\langle \partial n / \partial t \rangle = 0$  by taking the longitudinal part of  $\mathbf{v}(\mathbf{k})$  to be zero initially. With this additional requirement, we obtain

$$\begin{aligned} & imz(-iz + D_l k^2) n(\mathbf{k}, z) - k^2 p(\mathbf{k}, z) \\ &= -m(-iz + D_l k^2) n(\mathbf{k}) - iz \left[ \varepsilon(\mathbf{k}, z) - \frac{\varepsilon + p}{n} n(\mathbf{k}, z) \right] + \varkappa k^2 T(\mathbf{k}, z) \end{aligned} \quad (23)$$

$$-iz \left[ \varepsilon(\mathbf{k}, z) - \frac{\varepsilon + p}{n} n(\mathbf{k}, z) \right] + \varkappa k^2 T(\mathbf{k}, z) = - \left[ \varepsilon(\mathbf{k}) - \frac{\varepsilon + p}{n} n(\mathbf{k}) \right], \quad (24)$$

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

Notice that the energy equation involves the quantity

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

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

$$q(\mathbf{r}, t) = \varepsilon(\mathbf{r}, t) - \frac{\varepsilon + p}{n} n(\mathbf{r}, t) \quad (24')$$

will play an important role in our discussion. To understand this we recall the thermodynamic relation

$$T dS = dE + p dV,$$

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

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

and

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

Thus, at constant  $N$

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

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

We are of course permitted to use any convenient set of variables, and we shall work with the matter density  $n(k, z)$  and the above defined heat energy density  $q(k, z)$ . (We might have introduced instead the quantity  $T d(S/N) = de - \mu dn$  and called it the heat density.) Because the system is in local thermodynamic equilibrium, the temperature and pressure can be written as<sup>4</sup>

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

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

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

$$n(\mathbf{k}) = \frac{\partial n}{\partial p} \Bigg|_T p(\mathbf{k}) + \frac{\partial n}{\partial T} \Bigg|_p T(\mathbf{k}),$$

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

Written in terms of these new variables, (23) and (24) become

$$\left[ izm(-iz + D_l k^2) - k^2 \frac{\partial p}{\partial n} \Bigg|_S \right] n(\mathbf{k}, z) - k^2 \frac{V}{T} \frac{\partial p}{\partial S} \Bigg|_n q(\mathbf{k}, z) \\ = -m(-iz + D_l k^2) \left[ \frac{\partial n}{\partial p} \Bigg|_T p(\mathbf{k}) + \frac{\partial n}{\partial T} \Bigg|_p T(\mathbf{k}) \right], \quad (25)$$

$$\left[ -iz + \varkappa k^2 \frac{V}{T} \frac{\partial T}{\partial S} \Bigg|_n \right] q(\mathbf{k}, z) + \varkappa k^2 \frac{\partial T}{\partial n} \Bigg|_S n(\mathbf{k}, z) \\ = \frac{T}{V} \frac{\partial S}{\partial T} \Bigg|_p T(\mathbf{k}) + \frac{T}{V} \frac{\partial S}{\partial p} \Bigg|_T p(\mathbf{k}). \quad (26)$$

<sup>4</sup> Because our identification of  $q$  was made at fixed  $N$ , all the thermodynamic derivatives here and below must be taken at fixed  $N$ .

For superfluids, neglecting dissipative terms, (24') becomes

$$\begin{aligned} z^2 q(\mathbf{k}, z) - k^2 \frac{TS^2 \varrho_s}{mN^2 \varrho_n} & \left[ \frac{\partial T}{\partial n} \Big|_S n(\mathbf{k}, z) + \frac{V}{T} \frac{\partial T}{\partial S} \Big|_n q(\mathbf{k}, z) \right] \\ & = iz \frac{T}{V} \left[ \frac{\partial S}{\partial T} \Big|_p T(\mathbf{k}) + \frac{\partial S}{\partial p} \Big|_T p(\mathbf{k}) \right]. \end{aligned} \quad (26')$$

If we introduce the definitions

$$\begin{aligned} mnc_p & \equiv \frac{T}{V} \frac{\partial S}{\partial T} \Big|_p, & mnc_r & \equiv \frac{T}{V} \frac{\partial S}{\partial T} \Big|_n, \\ v^2 & \equiv \frac{TS^2}{m^2 N^2} \frac{\varrho_s}{\varrho_n c_r}, & \frac{\partial p}{\partial n} \Big|_S & = \frac{c_p}{c_r} \frac{\partial p}{\partial n} \Big|_T, \end{aligned} \quad (27)$$

we then obtain

$$\begin{aligned} n(\mathbf{k}, z) = p(\mathbf{k}) \frac{\partial n}{\partial p} \Big|_T & \frac{iz}{z^2 - c_1^2 k^2} \frac{c_1^2}{c_1^2 - c_2^2} \left[ 1 + \frac{c_2^2}{v^2} \left( 1 - \frac{c_p}{c_r} \right) - \frac{v^2}{c_1^2} \right] \\ & + T(\mathbf{k}) \frac{\partial n}{\partial T} \Big|_p \frac{iz}{z^2 - c_1^2 k^2} \frac{c_2^2}{c_2^2 - c_1^2} \\ & + \text{identical terms with } c_1 \leftrightarrow c_2, \end{aligned} \quad (28')$$

and

$$\begin{aligned} q(\mathbf{k}, z) = p(\mathbf{k}) \frac{T}{n} \frac{\partial n}{\partial T} \Big|_p & \frac{iz}{z^2 - c_1^2 k^2} \frac{c_2^2}{c_2^2 - c_1^2} \\ & + T(\mathbf{k}) mnc_p \frac{iz}{z^2 - c_1^2 k^2} \frac{c_2^2}{c_2^2 - c_1^2} \left[ 1 - \frac{v^2}{c_2^2} \frac{c_r}{c_p} \right] \\ & + \text{identical terms with } c_1 \leftrightarrow c_2. \end{aligned} \quad (29')$$

The two velocities  $c_1$  and  $c_2$  are determined by the determinant of the linear equations

$$z^4 - k^2 z^2 \left( v^2 + \frac{1}{m} \frac{\partial p}{\partial n} \Big|_S \right) + k^4 v^2 \frac{\partial p}{\partial n} \Big|_T = (z^2 - c_1^2 k^2) (z^2 - c_2^2 k^2) \quad (30)$$

and thus satisfy

$$c_1^2 + c_2^2 = v^2 + \frac{1}{m} \frac{\partial p}{\partial n} \Big|_S \quad c_1^2 c_2^2 = v^2 \frac{1}{m} \frac{\partial p}{\partial n} \Big|_T \quad (31)$$

When  $\nu = 0$ , we have the solutions  $c_1^2 = (1/m) \partial p / \partial n|_S$  and  $c_2^2 = 0$ . More generally, neglecting the difference between  $\partial p / \partial n|_S$  and  $\partial p / \partial n|_T$  we have  $c_2^2 = \nu^2$ . One of the roots represents undamped first sound, the other second sound. We can understand the significance of the root  $c_2^2 = 0$  when a system is not superfluid if we consider the effect of the dissipative terms in the normal fluid.

In particular, let us examine the situation at low temperatures where  $\partial p / \partial n|_S \approx \partial p / \partial n|_T \approx dp / dn$ . In this case, the differential equations for a normal fluid become decoupled and we have

$$n(\mathbf{k}, z) = -(-iz + D_l k^2) \frac{dn}{dp} p(\mathbf{k}) \left[ z^2 - \frac{1}{m} \frac{dp}{dn} k^2 + iz D_l k^2 \right]^{-1} \quad (28'')$$

and

$$q(\mathbf{k}, z) = \frac{T}{V} \frac{dS}{dT} T(\mathbf{k}) \left[ -iz + \varkappa k^2 \frac{V}{T} \frac{dT}{dS} \right]^{-1}. \quad (29'')$$

The first of these equations states that the density and pressure satisfy a damped sound wave equation

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

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

$$mc^2 = dp/dn$$

and the sound wave damping constant

$$I = D_l.$$

The second equation states that the temperature satisfies a diffusion equation

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

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

$$D_T = \varkappa \left| \frac{T}{V} \frac{dS}{dT} \right|.$$

That is, the solution, which is at  $z = 0$  when dissipative terms are neglected in a normal system, is an over-idealized representation of the heat conduction mode.

By examining the solutions for the normal fluid at arbitrary temperature, we find that, in the limit of small  $k$ ,

$$\begin{aligned} n(\mathbf{k}, z) &= p(\mathbf{k}) \left. \frac{\partial n}{\partial p} \right|_T \left( 1 - \frac{c_r}{c_p} \right) [-iz + D_T k^2]^{-1} \\ &\quad - p(\mathbf{k}) \left. \frac{\partial n}{\partial p} \right|_T \left[ I' \frac{c_r}{c_p} k^2 + D_T \left( 1 - \frac{c_v}{c_p} \right) k^2 - iz \frac{c_v}{c_p} \right] [z^2 - c^2 k^2 + iz\Gamma k^2]^{-1} \\ &\quad + T(\mathbf{k}) \left. \frac{\partial n}{\partial T} \right|_p [-iz + D_T k^2]^{-1} - T(\mathbf{k}) \left. \frac{\partial n}{\partial T} \right|_p D_T k^2 [z^2 - c^2 k^2 + iz\Gamma k^2]^{-1}, \\ q(\mathbf{k}, z) &= T(\mathbf{k}) mnc_p [-iz + D_T k^2]^{-1} + p(\mathbf{k}) \frac{T}{V} \left. \frac{\partial S}{\partial p} \right|_T [-iz + D_T k^2]^{-1} \\ &\quad - p(\mathbf{k}) \frac{T}{V} \left. \frac{\partial S}{\partial p} \right|_T D_T k^2 [z^2 - c^2 k^2 + iz\Gamma k^2]^{-1}, \end{aligned} \quad (28)$$

$$\mathbf{g}_t(\mathbf{k}, z) = \frac{mn\mathbf{v}_t(\mathbf{k})}{-iz + (\eta k^2/mn)}, \quad (32)$$

where  $c^2 = (1/m) \partial p / \partial n |_S \equiv c_1^2$  and the thermal diffusivity and the sound wave damping constants are

$$D_T = \alpha/mnc_p, \quad \Gamma = D_l + D_T[(c_p/c_v) - 1]. \quad (33)$$

## B. CORRELATION FUNCTION DESCRIPTION

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

Of course any force which disturbs the system from equilibrium will set up heat conduction and sound propagation processes, and, if we wait long enough, these will be the only persistent modes. However, if we are to infer the form of the correlation functions from the hydrodynamic equations, which are only true when the system is in local equilibrium, we must apply a disturbance that maintains the system in local equilibrium at short as well as long times. That is, we must employ an interaction Hamiltonian which disturbs the system in such a way that it is even initially in local equilibrium. A natural way of doing so is based on the observation that in a system moving with velocity  $\mathbf{v}$  the average of an operator,  $A$ , is

$$\langle A(\mathbf{r}, t) \rangle = \text{tr} [\varrho A(\mathbf{r}, t)]$$

$$\varrho = \exp \Xi [\text{Tr} \exp \Xi]^{-1}$$

$$\Xi = -\beta \left[ \mathcal{H}_0 - \mu \mathcal{N} + \frac{1}{2} m \mathbf{v}^2 \mathcal{N} - \int d\mathbf{r} \mathbf{g}(\mathbf{r}) \cdot \mathbf{v} \right].$$

The thermodynamics of the system are described by  $\beta$ ,  $\mu$ , and  $\mathbf{v}$ . If the velocity is small, the  $\mathbf{v}^2$  term may be neglected.

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

$$\varrho = \exp [-\beta(\mathcal{H} - \mu \mathcal{N})] \{ \text{Tr} \exp [-\beta(\mathcal{H} - \mu \mathcal{N})] \}^{-1}$$

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

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

In analogy with this expression we might expect that if we couple to the conserved variables with an interaction Hamiltonian containing three functions  $\delta\mu(\mathbf{r})$ ,  $\delta T(\mathbf{r})$ ,  $\delta\mathbf{v}(\mathbf{r})$  so that

$$\begin{aligned} \delta\mathcal{H}(t) = & - \int d\mathbf{r} \left\{ \frac{\delta T(\mathbf{r})}{T} [\epsilon(\mathbf{r}, t) - \mu n(\mathbf{r}, t)] + \delta\mu(r)n(\mathbf{r}, t) \right. \\ & \left. + \delta\mathbf{v}(r) \cdot \mathbf{g}(\mathbf{r}, t) \right\} e^{\epsilon t} \quad \text{for } t < 0 \\ & = 0 \quad \text{for } t > 0, \end{aligned} \tag{34}$$

we could describe a system in local thermodynamic equilibrium for all times less than zero and identify the function  $\delta\mathbf{v}(\mathbf{r})$  with the local velocity,  $T + \delta T(\mathbf{r})$  with the local temperature, and  $\mu + \delta\mu(\mathbf{r})$  with the local chemical potential. We could then use  $\delta\mathcal{H}$  as an interaction Hamiltonian for producing hydrodynamic flow.

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

$$\delta\langle A(\mathbf{r}, t) \rangle = \frac{\partial A}{\partial \mu} \Big|_{T, v} \delta\mu(\mathbf{r}) + \frac{\partial A}{\partial T} \Big|_{\mu, v} \delta T(\mathbf{r}) + \frac{\partial A}{\partial \mathbf{v}} \Big|_{\mu, T} \cdot \delta\mathbf{v}(\mathbf{r}) \quad \text{for } t < 0, \quad (35)$$

where the indicated derivatives are with respect to the variables  $\mu$ ,  $T$ , and  $\mathbf{v}$ .

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

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

According to the fluctuation-dissipation theorem the  $A$ - $n$  anticommutator is

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

We can calculate the thermodynamic derivative  $\partial A / \partial \mu$  obtaining

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

We may therefore write

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

Since the total number of particles is independent of time,  $\chi''_{A,n}(0, \omega)/\omega$

must be just a  $\delta$ -function at zero frequency. Therefore, we can make the replacement

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

and find

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

On the other hand we can use perturbation theory to calculate the response to the time-dependent disturbance (34). Then, in just the same way as we obtained (7), we find

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

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

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

If  $\delta\mu(\mathbf{r})$  contains only very small wave numbers or, equivalently, varies slowly in space, we may, under normal circumstances, replace the wave number  $k$  by zero. Assuming that this limit exists is tantamount to assuming that in the chosen ensemble there are no infinite ranged correlations, or fluctuations. It is valid in a one-component system only if it is normal. In a superfluid there are infinite range correlations and the limit  $k \rightarrow 0$  is ill defined for the velocity  $\delta\mathbf{v}$  and some operators  $A$  in a grand canonical ensemble. Likewise if the system has crystallized there will be a directional variation and ill-defined limits. Recalling this qualification we may write

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

or

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

thus justifying (35) which identifies the slowly varying parameters  $\delta\mu(\mathbf{r})$ ,  $\delta T(\mathbf{r})$ , and  $\delta\mathbf{v}(\mathbf{r})$  with changes in the chemical potential, slowly in space, temperature, and velocity.

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

$$dp = n d\mu + (S/V) dT = n d\mu + (\varepsilon + p - \mu n) dT/T$$

to define

$$p(\mathbf{k}) = n\mu(\mathbf{k}) + (\varepsilon + p - \mu n) T(\mathbf{k})/T.$$

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

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

Then, if we use the other relation to define

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

we have

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

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

Finally, we eliminate  $\delta\mu(\mathbf{r})$  from the disturbance by making use of this same identity. With these substitutions we have

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

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

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

We can now write the response of the system to the disturbance as

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

where

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

If we introduce our standard representation for the commutators of  $q$ ,  $n$  and the components of  $\mathbf{g}$ , we obtain, for times less than zero,

$$\begin{aligned} A(\mathbf{k}) &= \int \delta \langle A(\mathbf{r}, t) \rangle e^{-i\mathbf{k}\cdot\mathbf{r}} d\mathbf{r} \\ &= \int \frac{d\omega}{\pi} \frac{\chi''_{A,n}(\mathbf{k}, \omega)}{\omega} \frac{p(\mathbf{k})}{n} + \int \frac{d\omega}{\pi} \frac{\chi''_{A,q}(\mathbf{k}, \omega)}{\omega} \frac{T(\mathbf{k})}{T} \\ &\quad + \int \frac{d\omega}{\pi} \frac{\chi''_{A,\mathbf{g}}(\mathbf{k}, \omega)}{\omega} \cdot \mathbf{v}(\mathbf{k}), \end{aligned} \tag{36}$$

and for times greater than zero,

$$\begin{aligned} A(\mathbf{k}, z) &= \int_0^\infty dt e^{izt} \int d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} \delta \langle A(\mathbf{r}, t) \rangle \\ &= \int \frac{d\omega}{\pi i} \frac{\chi''_{A,n}(\mathbf{k}, \omega)}{\omega(\omega - z)} \frac{p(\mathbf{k})}{n} + \int \frac{d\omega}{\pi i} \frac{\chi''_{A,q}(\mathbf{k}, \omega)}{\omega(\omega - z)} \frac{T(\mathbf{k})}{T} \\ &\quad + \int \frac{d\omega}{\pi i} \frac{\chi''_{A,\mathbf{g}}(\mathbf{k}, \omega)}{\omega(\omega - z)} \cdot \mathbf{v}(\mathbf{k}). \end{aligned} \tag{37}$$

We are interested in the cases in which  $A(\mathbf{r}, t)$  is  $n(\mathbf{r}, t)$ ,  $q(\mathbf{r}, t)$ , or  $\mathbf{g}(\mathbf{r}, t)$ . Therefore, we shall discuss briefly the properties of the Fourier transforms of the commutators formed from these conserved operators.

From time-reversal invariance, rotational invariance, and the Hermitian nature of the operators, it follows that  $\chi''_{n,n}$ ,  $\chi''_{q,q}$ ,  $\chi''_{n,q}$ , and  $\chi''_{q,n}$  are each real odd functions of  $\omega$  and that

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

This equation expresses a reciprocity which was first discussed by Onsager.

The Fourier transform of the momentum-momentum commutator is a tensor, since it is an average of a direct product of two vectors. However, if a system is spatially invariant, the only tensor quantities of which  $\chi''_{g_i, g_j}(k, \omega)$  can be composed are the direct product  $\mathbf{k}_i \mathbf{k}_j$  and the unit matrix  $\delta_{i,j}$ . It is convenient in this case to express  $\chi''_{g_i, g_j}$  in terms of the linear combinations of these tensors,

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

The  $l$  and  $t$  stand for longitudinal and transverse since the division that we have selected breaks the tensor into two parts, one with components in the direction of  $k$ , the other whose dot product with  $k$  is zero. Both parts are real functions, odd in the frequency variable.

The conservation law

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

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

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

while a double application of this law gives

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

One more result of the number conservation law is

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

## C. THERMODYNAMIC AND HIGH FREQUENCY SUM RULES

By comparing expressions (35) and (36) we can deduce a variety of Kramers-Kronig relation sum rules of type (3) for the integrals of the various commutators. For example, we may take  $A(\mathbf{r}, t) = n(\mathbf{r}, t)$ . Since we have

$$n(\mathbf{k}) = \frac{\partial n}{\partial p} \Big|_T p(\mathbf{k}) + \frac{\partial n}{\partial T} \Big|_p T(\mathbf{k}),$$

we obtain

$$\lim_{k \rightarrow 0} \int \frac{d\omega}{\pi} \frac{\chi''_{n,n}(k, \omega)}{\omega} = \lim_{k \rightarrow 0} \chi_{n,n}(k) = n \frac{\partial n}{\partial p} \Big|_T \quad (37a)$$

$$\lim_{k \rightarrow 0} \int \frac{d\omega}{\pi} \frac{\chi''_{n,q}(k, \omega)}{\omega} = T \frac{\partial n}{\partial T} \Big|_p. \quad (37b)$$

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

$$\lim_{k \rightarrow 0} \int \frac{d\omega}{\pi} \frac{\chi''_{n,q}(k, \omega)}{\omega} = n \frac{T}{V} \frac{\partial S}{\partial p} \Big|_T = \frac{\partial n}{\partial T} \Big|_p, \quad (37c)$$

$$\lim_{k \rightarrow 0} \int \frac{d\omega}{\pi} \frac{\chi''_{q,q}(k, \omega)}{\omega} = \frac{T^2}{V} \frac{\partial S}{\partial T} \Big|_p = mnc_p T. \quad (37d)$$

For  $A(\mathbf{r}, t) = g(\mathbf{r}, t)$ , which is equivalent to

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

we obtain on letting  $k \rightarrow 0$  the expression

$$\lim_{k \rightarrow 0} \int \frac{d\omega}{\pi} \frac{\chi''_{g_i, g_j}(k, \omega)}{\omega} = \delta_{ij} mn.$$

This statement is certainly true if the system is spatially homogeneous and the process of letting  $k \rightarrow 0$  is uniquely defined. Without this assumption, but still taking the system spatially invariant, we have the more general statement

$$\lim_{k \rightarrow 0} \int \frac{d\omega}{\pi} \frac{\chi''_i(k, \omega)}{\omega} \equiv \varrho - \bar{\varrho}_s \equiv \bar{\varrho}_n \quad (37e)$$

but still, both generally and from our hydrodynamic analysis,

$$\int \frac{d\omega}{\pi} \frac{\chi''_i(k, \omega)}{\omega} = \int \frac{d\omega}{\pi} \frac{\omega^2 m^2}{k^2} \frac{\chi''_{n,n}(k, \omega)}{\omega} = mn. \quad (37f)$$

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

$$\lim_{k \rightarrow 0} \int \frac{d\omega}{\pi} \chi''_{j^q,g}(k, \omega) = 0.$$

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

$$\lim_{k \rightarrow 0} \int \frac{d\omega}{\pi} \frac{\omega^2}{mk^2} \chi''_{q,n}(k, \omega) = 0. \quad (37g)$$

Since the thermodynamic equations are only valid for small  $k$ , the sum rule (37a-g) are themselves only valid in the limit of vanishing wave number. There is however at least one exception to this restriction. Equation (37f), which expresses a sum rule on the density-density correlation function, is actually, valid for all  $k$ . This sum rule can be derived from an argument identical to the one that we used to get (10). That is to say, this result is a consequence of the exact commutation relation

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

which holds whenever there are velocity-independent forces. In fact, the sum rule (37f) is a famous result. In solid-state physics, it is usually referred to as the longitudinal  $f$ -sum rule. It has played a very important role in the discussion of the BCS theory of superconductivity. In neutron scattering studies, it is known as the Placzek sum rule.

In the classical limit, subject to the existence of the velocity correlation function Fourier transform or the absence of long-range order, (37e) is also exact for all  $k$ . It is intimately connected with the van Leeuwen theorem for charged systems and states that the orbital magnetic susceptibility of such systems vanishes. Landau has discussed how diamagnetic susceptibility can, in fact, appear in a quantum-mechanical system. In our language, this is a consequence of the fact that

$$\chi_t(k) - \chi_i(k) = \mathcal{O}(k^2)$$

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

Such quantum effects are even more drastic in superconducting systems and lead to the replacement of (37d) by (37c) in the limit  $k^2 \rightarrow 0$ . This replacement is reflected in the anomalous electromagnetic properties of the superconductor, most notably in the Meissner effect.

In superconductors, it is the parameter  $\bar{\varrho}_s$  which is normally used to define the superfluid density. In liquid helium it is this parameter which is measured ideally (neglecting vortex formation) in experiments with torsion balances. We have used the symbol  $\bar{\varrho}_s$  to designate the parameter determined from the reduced moment of inertia (or Meissner effect) in distinction to  $\varrho_s$  determined from the velocity of thermal waves. Their equality depends on the rigidity of the superfluid to vortex formation, in consequence of which, rotation sets only the normal fluid in motion.

#### D. CORRELATION FUNCTIONS AND DISSIPATIVE COEFFICIENTS

The statements (37a–e) are thermodynamic sum rules reflecting the equation of state (property 3). The statements (37f, g) reflect the conservation laws (property 1) in that they guarantee a vanishing weight as  $k \rightarrow 0$ . We may finally construct the hydrodynamic correlations functions and indicate the manner in which the phenomenological laws for normal fluids (property 2) appear in the correlation function description.

First we compare the hydrodynamical analysis and the correlation function description for  $t > 0$ , obtaining for normal fluids at low temperatures

$$\chi''_{q,q}(k, \omega) = \varkappa T k^2 \omega \left[ \omega^2 + \left( \varkappa k^2 \frac{V}{T} \frac{dT}{dS} \right)^2 \right]^{-1} \quad (38)$$

or, neglecting the dissipative terms entirely,

$$\chi''_{q,q}(k, \omega) = \pi \frac{T^2}{V} \frac{dS}{dT} \omega \delta(\omega) = 0 .$$

Correspondingly for the density correlation function we have

$$\chi''_{n,n}(k, \omega) = \frac{n k^4 \Gamma \omega}{m} \left[ \left( \omega^2 - \frac{1}{m} \frac{dp}{dn} k^2 \right)^2 + (\Gamma \omega k^2)^2 \right]^{-1} \quad (39)$$

which, upon neglecting dissipation, becomes

$$\chi''_{n,n}(k, \omega) = \frac{nk^2}{m} \pi \delta \left( \omega^2 - \frac{1}{m} \frac{dp}{dn} k^2 \right).$$

Finally, the crossed coefficient is given by

$$\chi''_{n,q}(k, \omega) = 0. \quad (40)$$

For a superfluid with no dissipation we would have instead

$$\begin{aligned} \chi''_{q,q}(k, \omega) &= mnc_p T \frac{c_1^2 c_2^2 k^2}{c_1^2 - c_2^2} \frac{\omega}{|\omega|} \left\{ \left( \frac{\nu^2}{c_2^2} \frac{c_v}{c_p} - 1 \right) \pi \delta(\omega^2 - c_1^2 k^2) \right. \\ &\quad \left. - \left( \frac{\nu^2}{c_1^2} \frac{c_v}{c_p} - 1 \right) \pi \delta(\omega^2 - c_2^2 k^2) \right\}, \end{aligned} \quad (38')$$

which reduces to the dissipationless normal fluid result when

$$c_1^2 = \frac{1}{m} \frac{\partial p}{\partial n} \Big|_S, \quad c_2^2 = \nu^2 = 0.$$

In the superfluid we would also have

$$\begin{aligned} \chi''_{n,n}(k, \omega) &= n \frac{\partial n}{\partial p} \Big|_T \frac{k^2}{c_1^2 - c_2^2} \frac{\omega}{|\omega|} \\ &\times \left\{ \left[ 1 + \frac{c_2^2}{\nu^2} \left( 1 - \frac{c_p}{c_v} \right) - \frac{\nu^2}{c_1^2} \right] c_1^4 \pi \delta(\omega^2 - c_1^2 k^2) \right. \\ &\quad \left. - \left[ 1 + \frac{c_1^2}{\nu^2} \left( 1 - \frac{c_p}{c_v} \right) - \frac{\nu^2}{c_2^2} \right] c_2^4 \pi \delta(\omega^2 - c_2^2 k^2) \right\}, \end{aligned} \quad (39')$$

which agrees with the normal fluid result when we make the replacement exact only at zero temperature  $c_p = c_v$ ,  $c_1^2 = (1/m) dp/dn$ ,  $c_2^2 = \nu^2$ . Finally in the superfluid we would have

$$\begin{aligned} \chi''_{q,n}(k, \omega) &= T \frac{\partial n}{\partial T} \Big|_p \frac{c_1^2 c_2^2 k^2}{c_1^2 - c_2^2} \frac{\omega}{|\omega|} \\ &\times \{ \pi \delta(\omega^2 - c_2^2 k^2) - \pi \delta(\omega^2 - c_1^2 k^2) \}. \end{aligned} \quad (40')$$

It follows from (38')–(40') that as  $T \rightarrow 0$  there is no oscillation at  $\omega = c_s k$ . The second sound velocity is defined, but the weight of the mode vanishes.

In a normal fluid at finite temperatures,  $n(k, z)$  and  $q(k, z)$  also contain contributions from both poles. As before, we can determine the absorptive susceptibilities which describe the long-wavelength, low-frequency response by comparison of (37) with (28) and (29). We obtain

$$\chi''_{q,q}(k, \omega) = \frac{nmc_p T D_T k^2 \omega}{\omega^2 + (D_T k^2)^2}, \quad (38'')$$

$$\begin{aligned} \chi''_{n,n}(k, \omega) &= \omega \operatorname{Re} [n(\mathbf{k}, z)/p(\mathbf{k})]_{z=\omega+i\epsilon} \\ &= n \frac{\partial n}{\partial p} \Big|_T \frac{[1 - (c_r/c_p)] D_T k^2 \omega}{\omega^2 + (D_T k^2)^2} \\ &\quad + n \frac{\partial n}{\partial p} \Big|_T \frac{\omega c^2 k^4 \Gamma(c_r/c_p)}{(\omega^2 - c^2 k^2)^2 + (\omega k^2 \Gamma)^2} \\ &\quad - n \frac{\partial n}{\partial p} \Big|_T \frac{D_T [1 - (c_r/c_p)] (\omega^2 - c^2 k^2) \omega k^2}{(\omega^2 - c^2 k^2)^2 + (\omega k^2 \Gamma)^2}, \end{aligned} \quad (39'')$$

$$\chi''_{n,q}(k, \omega) = \frac{\partial n}{\partial T} \Big|_p \left[ \frac{D_T k^2 \omega}{\omega^2 + (D_T k^2)^2} - \frac{D_T k^2 \omega (\omega^2 - c^2 k^2)}{(\omega^2 - c^2 k^2)^2 + (\omega k^2 \Gamma)^2} \right]. \quad (40'')$$

We also find, from (32),

$$\chi''_t(k, \omega) = \frac{\eta k^2 \omega}{\omega^2 + (\eta k^2/mn)^2}. \quad (41'')$$

We can sum up these results as follows: In the low wave number-low frequency limit, the correlation function composed of the transverse component of the momentum exhibits a diffusion structure with diffusivity given by the viscosity divided by the mass density,  $D_t = \eta/mn$ . The heat energy–heat energy correlation function also has a diffusion structure, but here the diffusivity is the thermal diffusivity,  $D_T = k/mnc_p$ . The density-density correlation function exhibits both this diffusion process and a damped sound wave propagation. The total weight of  $\chi''_{n,n}(\omega)$  is  $n(\partial p/\partial n)_T$ , of which a proportion  $(1 - c_r/c_p)$  comes from the diffusion process and a proportion  $c_r/c_p$  comes from the sound propagation. The heat energy–density correlation function also reflects both processes but the sound propagation contributes negligible weight to  $\chi''_{q,q}$ .

Again, by employing high-frequency, and low-frequency sum rules we can incorporate most of the desired structure in a rigorous fashion. Thus we may write, for the density correlation function for arbitrary  $k$ , the same statement we wrote for the magnetization density, namely,

$$\chi_{n,n}^{-1}(k, z) - \chi_{n,n}^{-1}(k) = -\frac{mz^2}{nk^2} + \frac{mz}{nk^2} \int \frac{d\omega'}{\pi} \frac{k^2 I(k, \omega')}{z - \omega'} . \quad (41)$$

Consequently, an exact form for  $n(\mathbf{k}, z)/p(\mathbf{k})$  is

$$\begin{aligned} \frac{n(\mathbf{k}, z)}{p(\mathbf{k})} \Big|_{z=\omega+i\epsilon} &= -\frac{1}{\omega} \left\{ \chi_{n,n}^{-1}(k) - \left[ \chi_{n,n}^{-1}(k) - \frac{m\omega^2}{nk^2} - i\omega\Gamma(k, \omega) \frac{m}{n} \right. \right. \\ &\quad \left. \left. + \frac{m\omega}{n} \mathcal{P} \int \frac{d\omega'}{\pi} \frac{\Gamma(k, \omega')}{\omega - \omega'} \right]^{-1} \right\} \end{aligned} \quad (42)$$

and

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

We should emphasize that Eqs. (41) and (42) are exact. However, whether or not these equations are useful depends critically upon the simplicity, or lack thereof, of the function  $I(k, \omega)$ . In the particular case of a low-temperature ordinary fluid, we have seen that the equations of fluid mechanics imply that  $\omega$  is slowly varying in  $\omega$  and  $k$  and that  $\chi_{n,n}(k) \rightarrow n (dp/dn)$ . At nonvanishing temperature our hydrodynamical analysis indicates that  $\Gamma(k, \omega)$  depends on the manner in which  $\omega$  and  $k$  approach zero, since  $\chi''_{n,n}(k, \omega)$  must include the thermal diffusion process indicated in (38''). That is to say,  $\Gamma$ , like  $\chi''$ , has different limits, depending on the ratio of  $\omega$  and  $k$  as they both approach zero. Specifically it can be shown that  $\Gamma$  must have a term which behaves like

$$\Gamma \cong \chi^{-1} \left( \frac{c_p}{c_v} - 1 \right) \frac{n}{m} D_T k^2 [\omega^2 + D_T^2 (c_p/c_v)^2 k^4]^{-1}$$

for small  $k$  and  $\omega$ , or in the dissipationless approximation that

$$\Gamma = \left( 1 - \frac{c_p}{c_v} \right) \frac{1}{m} \left. \frac{\partial p}{\partial n} \right|_T \pi \delta(\omega) .$$

For a superfluid in the same approximation,

$$\Gamma = \left(1 - \frac{c_p}{c_v}\right) \frac{1}{m} \frac{\partial p}{\partial n} \Big|_T \frac{\pi}{2} [\delta(\omega - vk) + \delta(\omega + vk)].$$

We comment briefly on the connection of the function  $\Gamma$  with the phenomenological analysis occasionally employed. Let us first notice that in a normal fluid the thermal contribution to  $\Gamma$  has poles at

$$\omega = \pm iD_T k^2 c_p / c_v = \pm ik^2 / mn c_v$$

corresponding to relaxation as a result of thermal conduction. In addition, the function  $\Gamma(k, \omega)$  contained the term which at low frequencies became a constant. This whole contribution vanished at high frequencies. We can represent both terms in the normal fluid by using a spectral representation<sup>5</sup> for  $\Gamma$  in which we take

$$\Gamma(k, \omega) = \sum_i \frac{\varphi_i(k)\tau_i(k)}{1 + \omega^2\tau_i^2(k)}.$$

(For a superfluid the poles of  $\Gamma$  cannot lie solely on the imaginary axis). Conversely, such a form would yield for  $\chi^{-1}(k, z)$  the frequently hypothesized form

$$\chi^{-1}(k, z) = -\frac{m}{n} \left[ \frac{z^2}{k^2} - c_\infty^2 - \sum_i \frac{\varphi_i(k)}{1 - iz\tau_i(k)} \right] \quad (43)$$

when  $z$  is in the upper half-plane. In this expression we have introduced

$$c_\infty^2 \equiv \frac{n}{m\chi(k)} + \sum \varphi_i(k).$$

When such a representation is exact or a good approximation, a description in terms of differential equation exhibiting irreversibility is appropriate.

<sup>5</sup> The reader who is familiar with the discussion of scattering amplitudes and the utility of analytically continuing the imaginary part of an amplitude (in the Mandelstam representation) will note that there is a similarity between that procedure and this discussion.

As in the discussion of spin diffusion we may write expressions for the transport coefficients in terms of the correlation functions of conserved quantities. For a normal fluid we have

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

so that the thermal conductivity can be expressed as

$$\kappa = \frac{\beta}{4T} \lim_{\omega \rightarrow 0} \left[ \lim_{k \rightarrow 0} \int d\mathbf{r} \int dt e^{-i\mathbf{k} \cdot \mathbf{r} + i\omega t} \langle \{j_x^q(\mathbf{r}, t), j_x^q(\mathbf{0}, 0)\} \rangle \right]. \quad (44a)$$

However, since momentum is conserved, we have

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

or

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

and also

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

or

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

Therefore, not only is the thermal conductivity given by expression (44a); it is also given by the much more general expression

$$\begin{aligned} \kappa = & \frac{\beta}{4T} \lim_{\omega \rightarrow 0} \left[ \lim_{k \rightarrow 0} \int d\mathbf{r} \int dt e^{-i\mathbf{k} \cdot \mathbf{r} + i\omega t} \right. \\ & \times \left. \langle \{j_x^q(\mathbf{r}, t + \lambda g_x(\mathbf{r}, t), j_x^q(\mathbf{0}, 0) + \lambda g_x(\mathbf{0}, 0)\} \rangle \right], \end{aligned} \quad (44b)$$

where  $\lambda$  is any constant. The choice  $\lambda = (\varepsilon + p)/(mn)$  gives us back the energy current  $j^\varepsilon$  so that  $\kappa$  is also

$$\kappa = \frac{\beta}{4T} \lim_{\omega \rightarrow 0} \left[ \lim_{k \rightarrow 0} \int d\mathbf{r} \int dt e^{-i\mathbf{k} \cdot \mathbf{r} + i\omega t} \langle \{j_x^\varepsilon(\mathbf{r}, t), j_x^\varepsilon(\mathbf{0}, 0)\} \rangle \right]. \quad (44c)$$

We finally indicate the standard Kubo-type expressions for the viscosity by employing the facts that

$$\lim_{\omega \rightarrow 0} \left[ \lim_{k \rightarrow 0} \frac{\omega}{k^2} \chi''_t(k, \omega) \right] = \eta \quad (44d)$$

and from

$$\lim_{\omega \rightarrow 0} \left[ \lim_{k \rightarrow 0} \frac{\omega}{k^2} \chi''_i(k, \omega) \right] = \lim_{\omega \rightarrow 0} \left[ \lim_{k \rightarrow 0} \frac{m^2 \omega^2}{k^4} \chi''_{n,n}(k, \omega) \right] = \frac{4}{3} \eta + \zeta \quad (44e)$$

Thus,

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

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

$$\begin{aligned} \eta \left( \delta_{ij} - \frac{1}{3} \frac{k_i k_j}{k^2} \right) + \zeta \frac{k_i k_j}{k^2} &= \frac{\beta}{4} \lim_{\omega \rightarrow 0} \left[ \lim_{k \rightarrow 0} \int d\mathbf{r} \int dt e^{-i\mathbf{k} \cdot \mathbf{r} + i\omega t} \right. \\ &\quad \times \sum_{nm} \left. \frac{k_n k_m}{k^2} \langle \{\tau_{im}(\mathbf{r}, t), \tau_{jn}(\mathbf{0}, 0)\} \rangle \right], \end{aligned} \quad (44f)$$

where  $\tau$  is the stress tensor.

In a superfluid these expressions for the dissipative coefficients must be augmented in various ways which are too lengthy for the blackboard and this set of lectures. Let me instead merely state that we have performed such analyses for superfluid systems, several component systems, and ferromagnetic systems and identified the correlation functions which determine their macroscopic parameters. The calculation of these transport coefficients by the various field theoretic perturbation techniques is then straightforward in principle. In practice, accurate calculations can only be performed in weakly coupled systems. For these systems, the same techniques may also be used to calculate the full correlation functions (for  $k$  and  $\omega \neq 0$ ) and thus the hydrodynamic equations, their range of validity, and the response of the system at higher frequencies and wavelengths. As might be expected, in rare systems, at very low

frequencies, the correlation function is just the resolvent kernel of a slightly modified linearized Boltzmann equation; this resolvent may alternatively be schematized as the summation of an infinite subset of the perturbation theory diagrams contributing to the correlation function. The very high frequency response described by the correlation function is more simply determined since it can be characterized and calculated in terms of successive collisions by perturbation theory. The transition from the one kind of behavior to the other occurs at a time, the collision time, which may be roughly characterized for weakly coupled systems in terms of the temperature, density, and interparticle potential.

Let me close these lectures with another opinionated statement. As far as I can see, the question of what is necessary for irreversibility (there are many conditions which will suffice), what the Boltzmann and various master equations describe, and other questions of this ilk are sufficiently well understood to make further belaboring pedantic. The same is true of general discussion of the irreversible equations of macroscopic physics. We can trace precisely how irreversible behavior emerges from the microscopically defined correlation functions (which still contain the reversible behavior) when we justifiably disregard an irrelevantly long time scale for a typical large system or an average of such systems (mathematically, by replacing densely spaced poles by a branch line.) We can also trace how the irreversible behavior which, in general, is not described by a differential equation in time (i.e., is non-Markovian) reduces approximately to irreversible behavior described by a differential equation in time. The necessary condition for this behavior, the existence of a continuation of the frequency-smoothed function containing only frequency poles (or exponentially decaying time dependence), will almost never be exactly satisfied but will frequently, e.g., in the macroscopic equations, be an excellent approximation, until such long times that the remaining decay is negligible. Moreover, independent of any such Markovian requirement, we have perfectly straightforward and well-defined procedures for calculating the correlation functions. By now there is little doubt that the most general, the best defined, and the most straightforward of these procedures is the Green's function technique in either its functional or equivalent diagrammatic form.

What remains to be learned is how to identify small parameters in the terms that contribute, so that we may accurately calculate correla-

tion functions for systems which are neither rare, nor weakly interacting for some other obvious reason. In what cases are simpler kinetic equations applicable? How do we calculate in dense liquids or other strongly interacting systems? And ultimately, how do we calculate correlation functions in the region of greatest correlation, near phase transition points? These are the only questions still unresolved — but then again they always were the really unresolved questions.

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