$$\ldots - \mathbf{k}_3 - \mathbf{k}_4).$$

Here $\mathbf{q} = \mathbf{k}_1 - \mathbf{k}_3 = \mathbf{k}_4 - \mathbf{k}_2$ is the momentum transfer in the interaction of $\mathbf{k}_1$, $\mathbf{k}_2$ by virtual scattering to $\mathbf{k}_3$, $\mathbf{k}_4$. Thus

$$\varepsilon_{12}^{(2)} = -m\left(\frac{4\pi e^2}{\Omega}\right)^2 \sum_{\mathbf{q}} \frac{1}{q^4} \cdot \frac{1}{\mathbf{q} \cdot (\mathbf{q} + \mathbf{k}_2 - \mathbf{k}_1)}. \tag{3}$$

The summation can be converted into an integral:

$$\sum \rightarrow \frac{\Omega}{(2\pi)^3} \int_0^\infty dq \, \frac{\pi}{q^4} \int_{-1}^{1} d\mu \, \frac{1}{1 + \mu\kappa}, \tag{4}$$

where $\kappa = |\mathbf{k}_2 - \mathbf{k}_1|/q$, and $\mu = \cos\theta$; here θ is measured from the direction of $\mathbf{k}_2 - \mathbf{k}_1$. The integral over $d\theta$ in (4) has the value

$$\frac{1}{\kappa} \log \frac{1 + \kappa}{1 - \kappa}.$$

The integral over dq involves $1/q^3$ and is seen to diverge at the lower limit $q \rightarrow 0$.

The removal of this divergence can be accomplished by diagrammatic analysis developed initially by Brueckner, and it turns out to be possible to sum in all orders the most important terms in the perturbation expansion. We develop the method of Brueckner in an appendix. There are simpler methods of handling the correlation energy problem, but the Brueckner analysis is revealing and important.

In the Brueckner method for calculating the correlation energy of an electron gas in the high density limit there are contributions from all orders of perturbation theory. This is caused by the long range of the coulomb interaction. In the actual physical situation we expect the coulomb interaction of a pair of electrons to appear as screened

SELF-CONSISTENT FIELD METHOD

We consider a single particle with the one-particle hamiltonian $H = H_0 + V(\mathbf{x},t)$, where $H_0 = p^2/2m$ and $V(\mathbf{x},t)$ is the self-consistent potential arising from the interaction with all other particles of the system. We let ρ denote the statistical operator represented by the *one-particle* density matrix; thus if ψ_m is a solution of the one-particle Hartree-Fock equation, with the expansion*

$$|m\rangle \equiv \psi_m(\mathbf{x},t) = \sum_{\mathbf{k}} |\mathbf{k}\rangle\langle\mathbf{k}|m\rangle \tag{5}$$

in terms of the eigenstates $|\mathbf{k}\rangle$ of H_0, then the density matrix is defined by

$$\langle\mathbf{k}'|\rho|\mathbf{k}\rangle \equiv \sum_m \langle\mathbf{k}'|m\rangle P_m \langle m|\mathbf{k}\rangle, \tag{6}$$

where P_m is the ensemble average probability that the state m is occupied. The equilibrium statistical operator ρ_0 of the unperturbed system ($V = 0$) has the property

$$\rho_0|\mathbf{k}\rangle = f_0(\varepsilon_{\mathbf{k}})|\mathbf{k}\rangle, \tag{7}$$

where $f_0(\varepsilon)$ is the statistical distribution function.

The equation of motion of $\rho = \rho_0 + \delta\rho$ is

$$i\dot{\rho} = [H,\rho], \tag{8}$$

or, if we linearize (8) by neglecting terms of order $V\,\delta\rho$,

$$i\,\delta\dot{\rho} \cong [H_0,\delta\rho] + [V,\rho_0]. \tag{9}$$

* This ρ is not identical with the particle density operator in the second quantization form introduced in Chapter 5.

Thus, on taking matrix elements between $|\mathbf{k}\rangle$ and $|\mathbf{k}+\mathbf{q}\rangle$,

$$(10)\quad i\frac{\partial}{\partial t}\langle\mathbf{k}|\delta\rho|\mathbf{k}+\mathbf{q}\rangle = \langle\mathbf{k}|[H_0,\delta\rho]|\mathbf{k}+\mathbf{q}\rangle + \langle\mathbf{k}|[V,\rho_0]|\mathbf{k}+\mathbf{q}\rangle$$
$$= (\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}+\mathbf{q}})\langle\mathbf{k}|\delta\rho|\mathbf{k}+\mathbf{q}\rangle + [f_0(\varepsilon_{\mathbf{k}+\mathbf{q}}) - f_0(\varepsilon_{\mathbf{k}})]V_{\mathbf{q}}(t),$$

where

$$(11)\quad V_{\mathbf{q}}(t) = \langle\mathbf{k}|V|\mathbf{k}+\mathbf{q}\rangle = \int d^3x\, V(\mathbf{x},t)e^{i\mathbf{q}\cdot\mathbf{x}}$$

is the qth fourier component of $V(\mathbf{x},t)$. In this section other fourier components are defined similarly.

The potential V is composed of an external potential V^0 plus a screening potential V^s related to the induced change δn in electron density. Thus V^0 might be the potential of a charged impurity and V^s the potential of the screening charges in the electron gas as induced by V_0. Now the induced change in electron density is

$$(12)\quad \delta n(\mathbf{x}) = \sum_m |m\rangle P_m\langle m| = \sum_m\sum_{\mathbf{k}\mathbf{k}'} |\mathbf{k}'\rangle\langle\mathbf{k}'|m\rangle P_m\langle m|\mathbf{k}\rangle\langle\mathbf{k}|$$
$$= \sum_{\mathbf{k}\mathbf{k}'} |\mathbf{k}'\rangle\langle\mathbf{k}|\langle\mathbf{k}'|\rho|\mathbf{k}\rangle = \sum_{\mathbf{q}} e^{-i\mathbf{q}\cdot\mathbf{x}}\sum_{\mathbf{k}'}\langle\mathbf{k}'|\delta\rho|\mathbf{k}'+\mathbf{q}\rangle = \sum_{\mathbf{q}} e^{-i\mathbf{q}\cdot\mathbf{x}}\delta n_{\mathbf{q}}.$$

The screening potential is related to $\delta n(\mathbf{x})$ by the poisson equation

$$(13)\quad \nabla^2V^s = -4\pi e^2\,\delta n;\qquad -q^2V^s_{\mathbf{q}}(t) = -4\pi e^2\langle\mathbf{k}|\delta n|\mathbf{k}+\mathbf{q}\rangle,$$

so that

$$(14)\quad V^s_{\mathbf{q}}(t) = \frac{4\pi e^2}{q^2}\sum_{\mathbf{k}'}\langle\mathbf{k}'|\delta\rho|\mathbf{k}'+\mathbf{q}\rangle.$$

On combining (10) and (14) we have the equation of motion in the absence of an external perturbation:

$$(15)\quad i\frac{\partial}{\partial t}\langle\mathbf{k}|\delta\rho|\mathbf{k}+\mathbf{q}\rangle = (\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}+\mathbf{q}})\langle\mathbf{k}|\delta\rho|\mathbf{k}+\mathbf{q}\rangle$$
$$+ \frac{4\pi e^2}{q^2}[f_0(\varepsilon_{\mathbf{k}+\mathbf{q}}) - f_0(\varepsilon_{\mathbf{k}})]\sum_{\mathbf{k}'}\langle\mathbf{k}'|\delta\rho|\mathbf{k}'+\mathbf{q}\rangle.$$

This equation is essentially the same as that obtained in the random phase approximation of Bohm and Pines.[2]

It is generally helpful to express the properties of the interacting electron gas in terms of the longitudinal dielectric constant $\epsilon(\omega,\mathbf{q})$. We may define the dielectric constant in various equivalent ways. The usual definition relates the polarization component $P_{\mathbf{q}}$ to the longi-

[2] For a review see D. Pines in *Solid state physics* 1 (1955).

tudinal electric field $E_{\mathbf{q}}$ by

$$(16)\quad E_{\mathbf{q}} + 4\pi P_{\mathbf{q}} = \epsilon(\omega,\mathbf{q})E_{\mathbf{q}} = D_{\mathbf{q}}.$$

We recall that $V = V^0 + V^s$ is the net potential, where V^0 is the external potential and V^s the potential of the induced charge. The relation (16) is equivalent to

$$(17)\quad V_{\mathbf{q}} - V^s_{\mathbf{q}} = \epsilon(\omega,\mathbf{q})V_{\mathbf{q}},$$

because the longitudinal polarization $P_{\mathbf{q}}$ gives rise to the induced electric field $-E^s_{\mathbf{q}}/4\pi$, where $E^s_{\mathbf{q}}$ is derived from the potential $V^s_{\mathbf{q}}$. Thus

$$(18)\quad \epsilon(\omega,\mathbf{q}) = V^0_{\mathbf{q}}/V_{\mathbf{q}},$$

the ratio of the applied potential to the effective potential. Further,

$$(19)\quad \operatorname{div}\mathbf{P} = e\,\delta n;\qquad -iqP_{\mathbf{q}} = e\,\delta n_{\mathbf{q}};\qquad eE_{\mathbf{q}} = -iqV_{\mathbf{q}},$$

so that

$$(20)\quad \epsilon(\omega,\mathbf{q}) = 1 + 4\pi\left(\frac{P_{\mathbf{q}}}{E_{\mathbf{q}}}\right) = 1 - 4\pi\frac{e^2\delta n_{\mathbf{q}}}{q^2V_{\mathbf{q}}},$$

where ω is the frequency associated with $V_{\mathbf{q}}$. The definition (16) of $\epsilon(\omega,\mathbf{q})$ is also used in (40) below, but there it is found convenient to consider an expression (42) for the dielectric constant in terms of the density of test and induced charges.

Now if $V_{\mathbf{q}}(t)$ acts as a time-dependent driving force in (10), we have

$$(21)\quad \langle\mathbf{k}|\delta\rho|\mathbf{k}+\mathbf{q}\rangle = \frac{f_0(\varepsilon_{\mathbf{k}+\mathbf{q}}) - f_0(\varepsilon_{\mathbf{k}})}{\varepsilon_{\mathbf{k}+\mathbf{q}} - \varepsilon_{\mathbf{k}} + \omega + is}V_{\mathbf{q}},$$

so that

$$(22)\quad \delta n_{\mathbf{q}} = \sum_{\mathbf{k}}\langle\mathbf{k}|\delta\rho|\mathbf{k}+\mathbf{q}\rangle = \sum_{\mathbf{k}}\frac{f_0(\varepsilon_{\mathbf{k}+\mathbf{q}}) - f_0(\varepsilon_{\mathbf{k}})}{\varepsilon_{\mathbf{k}+\mathbf{q}} - \varepsilon_{\mathbf{k}} + \omega + is}V_{\mathbf{q}}.$$

Finally we have the longitudinal dielectric constant (we should add to this the c.c.):

$$(23)\quad \boxed{\epsilon_{\mathrm{SCF}}(\omega,\mathbf{q}) = 1 - \lim_{s\to+0}\frac{4\pi e^2}{q^2}\sum_{\mathbf{k}}\frac{f_0(\varepsilon_{\mathbf{k}+\mathbf{q}}) - f_0(\varepsilon_{\mathbf{k}})}{\varepsilon_{\mathbf{k}+\mathbf{q}} - \varepsilon_{\mathbf{k}} + \omega + is}.}$$

This is an important result, from which we may calculate many properties of the system, including the correlation energy. The particular expression (23) is approximate because we started with a one-particle, and not a many-particle, hamiltonian. The approximation takes the electron to respond as a free particle to the average potential $V(\mathbf{x},t)$ in the system. The result is equivalent to that of the random phase approximation of Nozières and Pines. The transverse dielectric constant of an electron gas is the subject of Problem 16.3.

In the limit $\omega \gg k_F q/m$ the result (23) reduces to, with $\omega_p^2 = 4\pi ne^2/m$,

$$\epsilon(\omega,\mathbf{q}) \cong 1 - \frac{\omega_p^2}{\omega^2} + i\frac{e^2}{2\pi q^2}\int d^3k\, \mathbf{q}\cdot\frac{\partial f_0}{\partial \mathbf{k}}\,\delta\left(\omega + \frac{\mathbf{k}\cdot\mathbf{q}}{m}\right), \tag{24}$$

where we have used the relation

$$\lim_{s\to+0}\frac{1}{x+is} = \mathcal{P}\frac{1}{x} - i\pi\delta(x); \tag{25}$$

here $\mathcal{P}$ denotes principal part. At absolute zero the absorption given by $\mathcal{I}\{\epsilon\}$ vanishes if $\omega > k_F q/m$; we say this is the plasmon region. For $\omega < k_F q/m$ the imaginary part of ϵ is $2m^2e^2\omega/q^3$, at absolute zero. The real part of ϵ in (24) was obtained by writing

$$f_0(\varepsilon_{\mathbf{k}+\mathbf{q}}) - f_0(\varepsilon_{\mathbf{k}}) \cong \mathbf{q}\cdot\frac{\partial f_0}{\partial \mathbf{k}}, \tag{26}$$

and

$$\frac{1}{\omega + \mathbf{k}\cdot\mathbf{q}/m} \cong \frac{1}{\omega}\left(1 - \frac{\mathbf{k}\cdot\mathbf{q}}{m\omega}\right). \tag{27}$$

The real part of ϵ agrees with the result for the dielectric constant of a plasma at $q = 0$, already familiar from Chapter 3. The equations of motion (15) of the undriven system may be solved to give the approximate eigenfrequencies as functions of $\mathbf{q}$; the eigenfrequencies are just the roots of $\epsilon(\omega,\mathbf{q})$ in (23). The equations of motion are equivalent to those considered by K. Sawada, *Phys. Rev.* **106,** 372 (1957). The eigenvalues are of two types: for one type, $\omega \cong \varepsilon_{\mathbf{k}+\mathbf{q}} - \varepsilon_{\mathbf{k}}$, which is the energy needed to create an electron-hole pair by taking an electron from $\mathbf{k}$ in the fermi sea to $\mathbf{k} + \mathbf{q}$ outside the sea. The other type of eigenvalue appears for small $\mathbf{q}$ and is $\omega^2 \cong 4\pi ne^2/m$. Thus there are collective excitations as well as quasiparticle excitations, but the total number of degrees of freedom is $3n$.

The imaginary term in (24) gives rise to a damping of plasma oscillations called Landau damping; the magnitude of the damping involves the number of particles whose velocity component k_q/m in the direction $\mathbf{q}$ of the collective excitation is equal to the phase velocity ω/q of the excitation. These special particles ride in phase with the excitation and extract energy from it. This damping is important at large values of q, and the plasmons then are not good normal modes. In a degenerate fermi gas the maximum electron velocity is v_F; for q

such that $\omega_p/q > v_F$ there are no particles in the plasma that travel with the phase velocity, and consequently the imaginary part of $\epsilon(\omega,\mathbf{q})$ vanishes for $q < q_c = \omega_p/v_F$. Using (5.71) and (5.73), we have $q_c/k_F = 0.48r_s^{1/2}$. If we consider all modes having $q > q_c$ to be individual particle modes, then the ratio of the number of plasmon modes n' to the total number of degrees of freedom $3n$ is

$$\frac{n'}{3n} = \frac{1}{2\cdot 3}(0.48)^3 r_s^{3/2} = 0.018 r_s^{3/2}, \tag{28}$$

where the 2 in the denominator is from the spin. In sodium $r_s = 3.96$, and 14 percent of the degrees of freedom are plasmon modes.

We summarize: at low q the normal modes of the system are plasmons; at high q the normal modes are essentially individual particle excitations.

Plasmons in metals have been observed as discrete peaks in plots of energy loss versus voltage for fast electrons transmitted through thin metal films. More detailed evidence of the existence of plasmons is given by the observation[3] of photon radiation by excited plasmons. The dependence of this radiation on the angle of observation and on film thickness was predicted by R. A. Ferrell, *Phys. Rev.* **111,** 1214 (1958).

A comparison of the observed energy-loss peaks with the calculated plasma frequencies for the assumed valences are given in the accompanying table. The plasma frequencies given are corrected for the dielectric constant of the ion cores.

	Be	B	C	Mg	Al	Si	Ge
Valence	2	3	4	2	3	4	4
ω_{calc}	19	24	25	11	16	17	16 ev
ΔE_{obs}	19	19	22	10	15	17	17 ev

The comparison for the alkali metals is also striking because the inelastic-loss peaks are in close agreement with the threshold of optical transparency, as is expected.

	Li	Na	K
ω_{calc}	8.0	5.7	3.9 ev
ΔE	9.5	5.4	3.8 ev
ω_{opt}	8.0	5.9	3.9 ev

Thomas-Fermi Dielectric Constant. The Thomas-Fermi approximation to the dielectric constant of the electron gas is a quasistatic

[3] W. Steinman, *Phys. Rev. Letters* **5,** 470 (1960), *Z. Phys.* **163,** 92 (1961); R. W. Brown, P. Wessel, and E. P. Trounson, *Phys. Rev. Letters* **5,** 472 (1960).