

Electron-Ion Interactions and Many-Body Effects in Simple Metals*

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In this paper we derive expressions for a number of properties of simple metals, using a spatially local energy-independent pseudopotential to represent the electron-ion interaction. Quantities are expressed in terms of correlation functions for the homogeneous electron gas and matrix elements of the electron-ion pseudopotential; electron-electron interactions are included to all orders in perturbation theory, and electron-ion interactions to low order. First, we consider the long-wavelength finite-frequency dielectric function and generalize some results of Hopfield; the dielectric function is then used to derive expressions for optical properties, and the frequency and damping of long-wavelength plasma oscillations. Second, we consider the phonon spectrum; expressions for the phonon dynamical matrix are derived, taking into account the influence of the periodic ionic lattice on the motion of electrons. It is shown that to obtain results consistent with expressions for the elastic constants derived from expressions for the energy of the system calculated to the second order in the electron-ion interaction, one must include in the calculation of the phonon dynamical matrix some terms of third and fourth order in the electron-ion interaction. A detailed discussion of the long-wavelength behavior of the dynamical matrix is given.

I. INTRODUCTION

It is now possible to determine experimentally with fair precision a number of properties of metals; among these are the phonon spectrum, the elastic constants, the shape of the Fermi surface, the electrical resistivity, optical properties, and properties of plasmons. All these quantities depend both on the electron-ion interaction and also on the electron-electron interaction. For a number of metals, which we refer to as simple metals, the effects of the periodic ionic lattice are rather small and the Fermi surfaces of these metals differ little from spheres. To calculate the properties of such metals it is natural to treat the electron-ion interaction by perturbation theory, taking as the unperturbed system the homogeneous electron gas with a uniform background of positive charge. The electron-ion interaction is conveniently treated in the spirit of the pseudopotential method¹ first introduced by Phillips and Kleinman,² and by Antončík.³ Such calculations lead to expressions for physical quantities in terms of matrix elements of the electron-ion pseudopotential, and correlation functions for the homogeneous electron gas; these correlation functions cannot be calculated using low-order perturbation expansions in the electron-electron interaction since at metallic densities the electron gas is in the intermediate coupling regime; however, the properties of the homogeneous electron gas have previously been studied in some detail.⁴ Perturbation expansions in terms of the electron-ion interaction are particularly convenient since they enable one to take into account the effects of the periodic

ionic lattice without having to perform a band-structure calculation for the system; such low-order perturbation expansions will not, of course, give a correct account of effects, such as the interband optical absorption near threshold, which depend on the detailed structure of the excitation spectrum near Brillouin-zone boundaries.

In this paper we investigate a number of properties of simple metals on the assumption, commonly made in the past, that the electron-ion interaction may be represented by a spatially local energy-independent pseudopotential. The paper falls naturally into two sections; in the first we consider the long-wavelength finite-frequency dielectric function, for which we derive an expression exact to second order in the electron-ion interaction. This work is a generalization of the earlier work of Hopfield,⁵ who calculated the imaginary part of the dielectric function assuming the motion of the ions during an electronic process could be neglected. The calculations described here go beyond those of Hopfield in two respects; first, the motion of ions while an electronic process takes place is taken into account. Consequently, our results involve the dynamical form factor of the ions whereas Hopfield's depend only on the static form factor. This enables one to generalize Hopfield's calculation to frequencies below the ion plasma frequency. Second, expressions for the real part of the dielectric function are given. The latter enable one to derive rather compact expressions for the optical mass, and the shift due to band-structure effects of the long-wavelength plasmon frequency. The second part of the paper is

concerned with the calculation of phonon frequencies. In the past it has been customary to calculate the phonon dynamical matrix to second order in the electron-ion interaction and to neglect the effect of the periodic ionic lattice on the motion of the electrons. Here we take into account the effect of the periodic lattice on the motion of the electrons to second order in the electron-ion interaction. This approximation for the phonon dynamical matrix is consistent with expressions for the elastic constants found by differentiating the expression for the energy of the system calculated to second order in the electron-ion interaction. In the past it has often been assumed that the effective interaction between ions depends only on their separation⁶; this assumption is no longer valid when the effect of the periodic lattice on the motion of the electrons is taken into account.

In Sec. II we derive the expression for the long-wavelength finite-frequency dielectric function; applications of the result are considered in Sec. III. The calculation of the phonon dynamical matrix is described in Sec. IV, and in Sec. V we discuss in detail the long-wavelength behavior of the dynamical matrix. Section VI contains a discussion of the results for the dynamical matrix.

II. LONG-WAVELENGTH FINITE-FREQUENCY DIELECTRIC FUNCTION

In this section we calculate the long-wavelength finite-frequency dielectric function taking into account electron-electron interactions to all orders in perturbation theory and electron-ion interactions to second order. However, before turning to the details of the calculation we must discuss the definition of the dielectric function. Consider a system which is subjected to an external field of wave vector \vec{k} and angular frequency ω ; the current induced in the system will have frequency ω but, in general, will not be restricted to wave vector \vec{k} , except when the system is translationally invariant. In particular, if the system is periodic in space, the induced current will have components with wave vectors $\vec{k} + \vec{K}$, where \vec{K} is a reciprocal-lattice vector. In most cases the components of the current with wave vectors other than \vec{k} will not be directly measurable. For example, in measurements of optical properties \vec{k} corresponds to a wavelength of many thousands of lattice spacings whereas $\vec{k} + \vec{K}$ ($\vec{K} \neq 0$) corresponds to a wavelength of the order of the lattice spacing. The short-wavelength components of the current are not directly detectable and thus it is convenient to use a formalism in which they do not appear explicitly. We therefore define a conductivity tensor $\sigma_{\mu\nu}(\vec{k}, \omega)$ by the relation

$$j_{\mu}(\vec{k}, \omega) = \sum_{\nu} \sigma_{\mu\nu}(\vec{k}, \omega) E_{\nu}(\vec{k}, \omega), \quad (1)$$

where $\vec{j}(\vec{k}, \omega)$ is the component of the induced (electric) current having wave vector \vec{k} and frequency ω , and $\vec{E}(\vec{k}, \omega)$ is the component of the electric field having the same space and time dependence as the applied external field. In other words, $\sigma_{\mu\nu}(\vec{k}, \omega)$ gives the variation of $\vec{j}(\vec{k}, \omega)$ with $\vec{E}(\vec{k}, \omega)$ when the external field having wave number \vec{k} and frequency ω is varied, but all other components of the external field are held fixed.

The conductivity tensor is related to the current-current response tensor $\bar{\chi}_{\mu\nu}(\vec{k}, \omega)$ by the usual expression⁷

$$\sigma_{\mu\nu}(\vec{k}, \omega) = \frac{ie^2}{\omega} \left(\bar{\chi}_{\mu\nu}(\vec{k}, \omega) + \frac{n}{m} \delta_{\mu\nu} \right), \quad (2)$$

where n is the electron number density and m the electron mass. σ gives the response to the total electric field $\vec{E}(\vec{k}, \omega)$, not just to the external field. $\vec{E}(\vec{k}, \omega)$ is the sum of the external field and the self-consistent field having wave number \vec{k} and frequency ω ; consequently in calculating $\sigma(\vec{k}, \omega)$ one must omit all polarization processes involving a wave vector \vec{k} and frequency ω . $\bar{\chi}_{\mu\nu}$ is given by the relation

$$\bar{\chi}_{\mu\nu}(\vec{k}, \omega) = \frac{1}{i} \int_0^{\infty} dt e^{i\omega t} \langle [J_{\mu}(\vec{k}, t), J_{\nu}(-\vec{k}, 0)] \rangle, \quad (3)$$

where $\vec{J}(\vec{k}, t)$ is the spatial Fourier transform of the electron particle-current operator in the Heisenberg representation, $[,]$ denotes a commutator and $\langle \rangle$ a thermal average. In writing Eq. (3) we have omitted the ionic contribution to the electrical current since it is of order Zm/M compared to the electronic contribution. (Z is the atomic number and M the mass of an ion.)

In the usual way one may define a dielectric tensor by the relation

$$\epsilon_{\mu\nu}(\vec{k}, \omega) = \delta_{\mu\nu} + (4\pi i/\omega) \sigma_{\mu\nu}(\vec{k}, \omega) \quad (4)$$

$$= \delta_{\mu\nu} \left(1 - \frac{\omega_p^2}{\omega^2} \right) - \frac{4\pi e^2}{\omega^2} \bar{\chi}_{\mu\nu}(\vec{k}, \omega). \quad (5)$$

In deriving Eq. (5) from Eq. (4) we used Eq. (2) for $\sigma_{\mu\nu}$. Here $\omega_p \equiv (4\pi n e^2/m)^{1/2}$ is the electron plasma frequency.

In the remainder of this section we shall consider only the finite-frequency long-wavelength dielectric function. For cubic and isotropic materials, to which we confine our attention, the finite-frequency dielectric function is a scalar in the limit $\vec{k} \rightarrow 0$; one can therefore write the dielectric function in the form

$$\epsilon(0, \omega) = 1 - \frac{\omega_p^2}{\omega^2} - \frac{4\pi e^2}{\omega^2} \eta_{\mu} \eta_{\nu} \bar{\chi}_{\mu\nu}(0, \omega), \quad (6)$$

where $\vec{\eta}$ is an arbitrary unit vector.

Next we turn to the derivation of expressions for $\bar{\chi}_{\mu\nu}(0, \omega)$. The Hamiltonian for the system may be

written in the form

$$H = H_{e1} + H_{ion} + H_{int} \quad (7)$$

where H_{e1} is the Hamiltonian of the electrons, including electron-electron interactions, H_{ion} is the Hamiltonian of the ions, and H_{int} is the electron-ion interaction; the latter is given by the expression

$$H_{int} = \sum_{\vec{k}} V_{\vec{k}} \rho_{\vec{k}}^{\dagger} \rho_{\vec{k}} \quad (8)$$

Here $\rho_{\vec{k}}^{\dagger}$ and $\rho_{\vec{k}}$ are the spatial Fourier transforms of the ion and electron number density operators, and $V_{\vec{k}}$ is the Fourier transform of the electron-ion pseudopotential, which, as we stated in the introduction, is assumed to be spatially local and energy independent. For simplicity, we also assume that there is only a single species of ion in the system. In general, we shall neglect the transverse magnetic interactions between electrons since this gives rise to contributions of order v_F^2/c^2 compared to the contributions from the Coulomb interactions.⁸ (Here v_F is the electron Fermi velocity.)

$\bar{\chi}_{\mu\nu}(0, \omega)$ has a spectral representation of the usual form in terms of the eigenstates of the Hamiltonian (7),

$$\bar{\chi}_{ii}(0, \omega) = \sum_{mn} \frac{e^{-\beta E_n}}{\Lambda} |(J_i)_{mn}|^2 \frac{2\omega_{mn}}{\omega^2 - \omega_{mn}^2} \quad (9)$$

m and n are eigenstates of the combined electron-ion system and their energies are given by E_m and E_n . Here $\omega_{mn} = E_m - E_n$,⁹ Λ is the partition function for the system, and $\beta = 1/k_B T$, where k_B is Boltzmann's constant and T the temperature. \vec{J}_{mn} is the matrix element of the $\vec{k} = 0$ component of the electron-current operator; this may be evaluated directly by using the equation of motion for J ,

$$[\vec{H}, \vec{J}]_{mn} = \hbar \omega_{mn} (\vec{J})_{mn} \quad (10)$$

$$[\vec{H}, \vec{J}]_{mn} = \sum_{\vec{k}} (\vec{k}/m) V_{\vec{k}} (\rho_{\vec{k}}^{\dagger} \rho_{\vec{k}}^{\dagger})_{mn} \quad (11)$$

On substituting Eq. (11) into Eq. (9) one finds¹⁰

$$\bar{\chi}_{ii}(0, \omega) = - \sum_{\vec{k}, \vec{k}'} \frac{k_i k'_i}{m^2 \omega^2} V_{\vec{k}} V_{\vec{k}'} [\Xi(\vec{k}, \vec{k}'; \omega) - \Xi(\vec{k}, \vec{k}'; 0)] \quad (12)$$

where

$$\Xi(\vec{k}, \vec{k}'; \omega) = \sum_{m,n} \frac{(e^{-\beta E_n} - e^{-\beta E_m})}{\Lambda} (\rho_{\vec{k}}^{\dagger} \rho_{\vec{k}}^{\dagger})_{nm} (\rho_{\vec{k}'}^{\dagger} \rho_{\vec{k}'}^{\dagger})_{mn} \frac{1}{\omega - \omega_{mn}} \quad (13)$$

We note that in the above calculation $\vec{k} = 0$ polarization processes have been excluded, as required, by neglecting transverse magnetic interactions and ignoring effects of the boundaries of the specimen.

Equations (6), (12), and (13) may be combined to give a very general result for the long-wavelength

dielectric function, including all the effects of band structure, electron-electron interactions, and the dynamics of the ions. The remainder of this section is devoted to a discussion of approximations for Ξ . Consider first of all a situation in which the ions are arranged in a periodic array and are static. $\rho_{\vec{k}}^{\dagger}$ may then be replaced by $\sum_{\vec{R}} n_I \delta_{\vec{k}, -\vec{R}, 0}$, where n_I is the number density of ions and \vec{K} is a reciprocal-lattice vector. The expression for $\bar{\chi}_{ii}(0, \omega)$ then reduces to

$$\bar{\chi}_{ii}(0, \omega) = - \sum_{\vec{K}, \vec{K}'} (K_i K'_i / m^2 \omega^2) n_I^2 V_{\vec{K}} V_{\vec{K}'} \times [\bar{\chi}(\vec{K}, \vec{K}'; \omega) - \bar{\chi}(\vec{K}, \vec{K}'; 0)] \quad (14)$$

where

$$\bar{\chi}(\vec{K}, \vec{K}'; \omega) = \sum_{m,n} \frac{e^{-\beta E_n} - e^{-\beta E_m}}{\Lambda} \frac{(\rho_{\vec{K}})_{nm} (\rho_{\vec{K}'})_{mn}}{\omega - \omega_{mn}} \quad (15)$$

is the density-density correlation function for electrons moving in the periodic potential of the ions. Equation (14) gives an exact description of the dielectric properties of electrons moving in a periodic potential and includes all band-structure effects. We note that two powers of the electron-ion interaction appear explicitly in Eq. (14); thus if band-structure effects are expected to be small, one may evaluate $\bar{\chi}_{ii}$ by replacing $\bar{\chi}(\vec{K}, \vec{K}'; \omega)$ in Eq. (14) by its value for the homogeneous electron gas. One then arrives at the following expression for the dielectric function:

$$\epsilon(0, \omega) = 1 - \frac{\omega_p^2}{\omega^2} - \frac{\omega_p^2}{\omega^4} \sum_{\vec{K}} \frac{n_I K^2}{3mZ} V_{\vec{K}}^2 [\bar{\chi}(\vec{K}, \omega) - \chi(\vec{K}, 0)] \quad (16)$$

Here $\chi(\vec{K}, \omega)$ is the density-density correlation function for the electron gas in the absence of the periodic potential. Of course, this approximation will not give a good account of the dielectric function near band gaps; to describe the effect of band gaps, multiple scattering of electrons by the lattice must be taken into account.¹¹

The next more complicated approximation for Ξ is obtained by neglecting correlations between electronic and ionic densities. From Eqs. (12) and (13) one then finds

$$\begin{aligned} \bar{\chi}_{\mu\nu}(0, \omega) = & \sum_{\vec{k}, \vec{k}'} \frac{k_{\mu} k'_{\nu}}{m^2 \omega^2} V_{\vec{k}} V_{\vec{k}'} \int \frac{d\omega'}{2\pi} \frac{d\omega''}{2\pi} \frac{(1 - e^{-\beta(\omega' + \omega'')})}{(1 - e^{-\beta\omega'})} \\ & \times S(\vec{k}, \vec{k}'; \omega'') \text{Im} \bar{\chi}(-\vec{k}, -\vec{k}'; \omega') \\ & \times \left(\frac{1}{\omega - \omega' - \omega''} + \frac{1}{\omega' + \omega''} \right) \quad (17) \end{aligned}$$

where

$$S(\vec{k}, \vec{k}'; \omega) \equiv \int_{-\infty}^{\infty} dt \langle \rho_{\vec{k}}^{\dagger}(t) \rho_{\vec{k}'}^{\dagger}(0) \rangle e^{i\omega t} \quad (18)$$

and $\bar{\chi}(\vec{k}, \vec{k}'; \omega)$ is the density-density correlation

function for the electrons (interacting with the ions).

The ions affect the electronic correlation functions in a number of different ways. First, the periodic ionic lattice gives rise to band-structure effects; second, phonons modify the electron density of states and effective interactions; and, third, phonons and disorder damp the motion of electrons. Phonon modification of the proper electronic response functions is negligible when either $\omega \gg \Omega_p$, or $k_B T \gg \hbar \Omega_p$, where $\Omega_p = [4\pi n_A (Ze)^2 / M]^{1/2}$ is the ion plasma frequency.¹² We also note that the electron density-density response function is considerably modified by ionic screening when $\omega \lesssim \Omega_p$. However, the contributions to $\bar{\chi}_{\mu\nu}$ which come from terms in (17) involving screening of the electronic motion by phonons are cancelled by other contributions to $\bar{\chi}_{\mu\nu}$ obtained by decoupling Ξ [Eq. (13)] as a product of two electron-density-ion-density correlation functions. Yet another regime in which phonon renormalization effects are negligible is when $\omega \ll \Omega_p$; the proper electronic density-density response function is not affected by phonon effects provided $\omega \ll \Omega_p$ even if $k_B T \lesssim \hbar \Omega_p$.¹²

Damping of the electrons will be unimportant provided $\omega \gg 1/\tau$, where $1/\tau$ is a typical electron collision frequency; when $\omega \lesssim 1/\tau$ multiple scattering of electrons by ions must be taken into account. Thus in (17), $\bar{\chi}(\vec{k}, \vec{k}'; \omega')$ may be replaced by $\chi(k, \omega') \times \delta_{\vec{k}+\vec{k}',0}$, its value for the homogeneous electron gas in the absence of electron-ion interactions, provided (i) band-structure effects are small, (ii) either $k_B T \gg \hbar \Omega_p$, or $\omega \gg \Omega_p$, or $\omega \ll \Omega_p$, and (iii) $\omega \gg 1/\tau$. Making this replacement in (17) one finds

$$\begin{aligned} \bar{\chi}_{\mu\nu}(0, \omega) = & - \sum_{\vec{k}} \frac{k_\mu k_\nu}{m^2 \omega^2} V_k^2 \int \frac{d\omega' d\omega''}{2\pi^2} \\ & \times \frac{1 - e^{-\beta(\omega' + \omega'')}}{1 - e^{-\beta\omega'}} S(\vec{k}, \omega'') \text{Im}\chi(k, \omega') \\ & \times \left(\frac{1}{\omega - \omega' - \omega''} + \frac{1}{\omega' + \omega''} \right); \quad (19) \end{aligned}$$

$S(\vec{k}, \omega) \equiv S(\vec{k}, -\vec{k}; \omega)$ is the well-known van Hove scattering function determined in neutron-scattering experiments.¹³ In many applications $\hbar\omega \gg k_B T$, and the ratio of the thermal factors in (19) may be replaced by unity to give

$$\begin{aligned} \bar{\chi}_{\mu\nu}(0, \omega) = & \sum_{\vec{k}} \frac{k_\mu k_\nu}{m^2 \omega^2} V_k^2 \int \frac{d\omega'}{2\pi^2} S(\vec{k}, \omega') \\ & \times [\chi(k, \omega - \omega') - \chi(k, -\omega')]. \quad (20) \end{aligned}$$

Finally, when $\omega \gg \Omega_p$ and $\text{Im}\chi(k, \omega)$ is a slowly varying function of ω , it is a good approximation

to replace $\chi(k, \omega - \omega') - \chi(k, -\omega')$ by its value at $\omega' = 0$ and to remove it from the integral. This gives

$$\epsilon(0, \omega) = 1 - \frac{\omega_p^2}{\omega^2} - \frac{\omega_p^2}{\omega^4} \sum_{\vec{k}} \frac{k^2}{3m} \frac{V_k^2}{Z} S(\vec{k}) [\chi(k, \omega) - \chi(k, 0)], \quad (21)$$

where

$$S(\vec{k}) = (1/n_I) \int_{-\infty}^{\infty} (d\omega/2\pi) S(\vec{k}, \omega) \quad (22)$$

is the static ionic form factor. The imaginary part of Eq. (21) is identical with the expression derived by Hopfield.⁵

The approximation made above is essentially equivalent to the Born approximation – just two electron-ion interactions are taken into account explicitly. Are there more complicated contributions to Ξ [Eq. (13)] of any importance? We have examined a number of such contributions but have found none which are appreciable when $\omega \gg 1/\tau$ and the pseudopotential is weak; we are led to speculate that such contributions are indeed negligible. In the case of disordered systems, such as liquid metals, there could conceivably be contributions due to the scattering of electrons from correlated clusters of ions; the size of such contributions can only be obtained from detailed calculations. We also note that to describe phonon-aided interband processes one must take into account contributions to Ξ which contain the electron-ion interaction.¹⁴

III. APPLICATION OF RESULTS FOR $\epsilon(0, \omega)$

In this section we use the results of Sec. II to derive expressions for the optical mass, the optical absorption, the shift in the plasma frequency due to band-structure effects, and the damping of plasmons.

In a solid there are two sorts of contribution to $S(\vec{k}, \omega)$. First, there are zero frequency components when \vec{k} is equal to a reciprocal-lattice vector, and second, there is an incoherent background due to motion of the ions and to disorder. The former give rise to interband effects, whereas the latter give rise to intraband effects. Let us first of all examine $\text{Im}\epsilon(0, \omega)$ at frequencies below the threshold for interband transitions and show how our result is related to results obtained using a phenomenological quasiparticle transport equation. At low frequencies ($\omega \ll v_F k$) the leading contribution to $\text{Im}\chi(k, \omega)$ is proportional to ω for $0 < k < 2k_F$. (k_F is the Fermi momentum.) This contribution comes from single quasiparticle-quasihole states, and may be calculated using the methods described by Langer.¹⁵ One finds

$$\begin{aligned} \text{Im}\chi(k, \omega) = & \pi \int \sum_{\vec{p}} |\Lambda_4(\vec{p}, \vec{p} + \vec{k}; \epsilon, \epsilon')|^2 A_{\vec{p}}(\epsilon) A_{\vec{p}+\vec{k}}(\epsilon') \\ & \times [n(\epsilon') - n(\epsilon)] (d\epsilon/2\pi) (d\epsilon'/2\pi) \delta(\omega - \epsilon' + \epsilon). \quad (23) \end{aligned}$$

Here \vec{p} and $(\vec{p} + \vec{k})$ are the momenta of the initial and final quasiparticles, ϵ and ϵ' are energy variables, $n(\epsilon)$ is the Fermi function, $A_{\vec{p}}(\epsilon)$ is the spectral density of the single-particle propagator, and $\Lambda_4(\vec{p}, \vec{p} + \vec{k}; \epsilon, \epsilon')$ is the density vertex part.¹⁶ For $p \approx k_F$, $A_p(\epsilon)$ consists of two parts – a sharply peaked part (the quasiparticle part) and an incoherent background. As $\omega \rightarrow 0$ only the quasiparticle part contributes to Eq. (23) and one finds

$$\text{Im}\chi(\vec{k}, \omega) = -\frac{m^{*2} \omega}{2\pi k} |a\Lambda_4(\vec{p}, \vec{p} + \vec{k}; 0, 0)|^2, \quad (24)$$

where m^* is the effective mass of a quasiparticle, a is the renormalization constant for particles on the Fermi surface, and the momenta \vec{p} and $\vec{p} + \vec{k}$ are to be put equal to k_F . Substituting (24) into (19) and using (8) one finds

$$\text{Im}\epsilon(0, \omega) = \frac{\omega_p^2}{\omega^3} \frac{m^*}{m} \frac{2}{3} \frac{m^*}{n} \frac{(1 - e^{-\beta\omega})}{\beta\omega} \int_0^{2k_F} \frac{k^3 dk}{(2\pi)^3} |V_k^{\text{eff}}|^2 \times \int \frac{d\omega' d\omega''}{2\pi} \frac{S(k, \omega') \beta \omega''}{1 - e^{-\beta\omega''}} \delta(\omega - \omega' - \omega''), \quad (25)$$

where

$$V_k^{\text{eff}} = a\Lambda_4(\vec{p}, \vec{p} + \vec{k}; 0, 0) V_k. \quad (26)$$

As Heine, Nozières, and Wilkins point out, V_k^{eff} is the effective interaction between a quasiparticle and an ion; this effective potential also enters calculations of the band structure.¹⁶

If $\epsilon(0, \omega)$ is calculated using a quasiparticle transport equation and the collision term is approximated using a single relaxation time, one finds

$$\epsilon(0, \omega) = 1 - \frac{\omega_p^2}{\omega[\omega + i(m^*/m)(1/\tau_{\text{tr}})]}, \quad (27)$$

where τ_{tr} is the transport relaxation time. For $\omega \gg 1/\tau_{\text{tr}}$, (25) has the same form as (27) provided one makes the identification

$$\frac{1}{\tau_{\text{tr}}} = \frac{2}{3} \frac{m^*}{n} \frac{1 - e^{-\beta\omega}}{\beta\omega} \int_0^{2k_F} \frac{k^3 dk}{(2\pi)^3} V_k^{\text{eff}^2} \int_{-\infty}^{\infty} \frac{d\omega'}{2\pi} \frac{d\omega''}{2\pi} S(k, \omega') \times \frac{\beta\omega''}{e^{\beta\omega''} - 1} \delta(\omega - \omega' - \omega''). \quad (28)$$

The expression for $\epsilon(0, \omega)$, Eq. (25), is valid only for $\omega \gg 1/\tau_{\text{tr}}$. However, if one uses Eq. (28) to define a (frequency-dependent) relaxation time even for $\omega \lesssim 1/\tau_{\text{tr}}$, $1/\tau_{\text{tr}}$ in the limit $\omega \rightarrow 0$ agrees with Baym's expression for the dc relaxation time.¹⁷ However, two points should be noted. First, although the basic approximation for the scattering (Born approximation) is the same in the two calculations, Baym's expression for the relaxation time is a variational estimate intended to give correctly the electrical conductivity in the hydrodynamic regime ($\omega\tau_{\text{tr}} \ll 1$), whereas the relaxation time de-

finied by Eq. (28) is appropriate for the collisionless regime ($\omega\tau_{\text{tr}} \gg 1$). The fact that the simplest variational estimates of relaxation times in the hydrodynamic regime agree with the exact relaxation time in the collisionless regime is known from work on other problems, such as the attenuation of zero sound and first sound in Fermi liquids.¹⁸

Let us now turn to interband contributions to $\epsilon(0, \omega)$. The contribution to $S(\vec{k})$ coming from the periodic lattice has the form $n_I \sum_{\vec{K}} \delta_{\vec{k}, \vec{K}}$, if one neglects for simplicity the Debye-Waller factor. Substituting this expression into Eq. (21), which is a valid expression at optical frequencies, one finds

$$\epsilon(0, \omega)_{\text{interband}} = 1 - \frac{\omega_p^2}{\omega^2} - \frac{\omega_p^2}{\omega^4} \sum_{\vec{K}} \frac{K^2}{3m} \frac{n_I}{Z} \times V_K^2 [\chi(\vec{K}, \omega) - \chi(\vec{K}, 0)]. \quad (29)$$

For values of ω large compared with $1/\tau_{\text{tr}}$ but small compared with the interband threshold, $\epsilon(0, \omega)$ is often expressed in terms of an optical mass m_B , defined by the equation

$$\text{Re}\epsilon(0, \omega) = 1 - \frac{m}{m_B} \frac{\omega_p^2}{\omega^2}, \quad \omega \gg \frac{1}{\tau_{\text{tr}}}. \quad (30)$$

Assuming that $1/\tau_{\text{tr}}$ is small compared to the characteristic frequency over which $\chi(K, \omega)$ varies, and using (29) and (30), we find

$$\frac{m}{m_B} = 1 + \sum_{\vec{K}} \frac{K^2}{6m} \frac{n_I}{Z} V_K^2 \frac{\partial^2 \chi(K, 0)}{\partial \omega^2}. \quad (31)$$

If $\chi(K, \omega)$ is calculated in much the same spirit as we calculated $\text{Im}\chi(k, \omega)$ earlier, taking into account only single quasiparticle-quasihole states, Eq. (31) reduces to the usual second-order perturbation theory expression for the average effective mass of the electrons, the effective electron-lattice interaction again being given by V_K^{eff} [Eq. (26)]. However, Eq. (31) is valid even if more general expressions for $\chi(K, \omega)$ are used.

The interband optical absorption may be determined from Eq. (29), and the result agrees with that of Hopfield,⁵

$$\text{Im}\epsilon(0, \omega) = -\frac{\omega_p^2}{\omega^4} \sum_{\vec{K}} \frac{K^2}{3m} \frac{n_I}{Z} V_K^2 \text{Im}\chi(K, \omega). \quad (32)$$

If one uses random-phase approximation (RPA) or Hubbard expressions for the response functions of the homogeneous electron gas⁴ both to infer values of V_K from Fermi-surface data [see Eq. (26)] and to estimate $\chi(K, \omega)$, Eq. (32) does not give a satisfactory account of the experimental data. These difficulties have been ascribed to the inadequacy of the assumption that the pseudopotential is spatially local and energy independent.¹⁹

Finally, we discuss the frequency and damping of long-wavelength plasmons. These are given by

the zeros of $\epsilon(0, \omega)$, which occur at a frequency $\omega' = \omega_p' - i\omega_2$, where, to second order in the pseudo-potential,

$$\frac{\omega_p'}{\omega_p} = 1 + \sum_{\vec{k}} \frac{k^2}{6m} \frac{V_k^2}{\omega_p^2} S(\vec{k}) [\text{Re}\chi(k, \omega_p) - \chi(k, 0)], \quad (33)$$

$$\frac{\omega_2}{\omega_p} = \sum_{\vec{k}} \frac{k^2}{6m} \frac{V_k^2}{\omega_p^2} S(\vec{k}) \text{Im}\chi(k, \omega_p). \quad (34)$$

Equation (33) does not contain the effects of the polarizability of the core electrons; these are discussed by Pines²⁰ and also by Hedin.²¹ In deriving (33) and (34) we used Eq. (21) which is valid since $\omega_p \gg \Omega_p$. To determine the frequency and damping of plasmons with finite wave numbers one must calculate directly $\bar{\chi}_{\mu\nu}(k, \omega)$. The contributions of second order in the electron-ion interaction can be expressed in terms of a four-point function for the homogeneous electron gas. However, this correlation function cannot generally be expressed in terms of two-point functions as it can in the long-wavelength limit.

IV. EFFECTS OF PERIODICITY ON PHONON SPECTRUM

In this section we consider how modifications of the electron gas by the periodic ionic lattice affect the phonon spectrum. Consider a system containing n_I ions per unit volume. We assume the equilibrium positions of the ions lie on a periodic lattice. The electron-ion interaction [Eq. (8)], when expanded to second order in the phonon operators $q_{\vec{k}}$, has the following form:

$$H_{\text{int}} = \sum_{\vec{R}} \langle \rho_{\vec{R}} \rangle V_{\vec{R}} \rho_{\vec{R}}^\dagger - i \sum_{\vec{k}, \vec{K}} \left(\frac{n_I}{M} \right)^{1/2} (\vec{k} + \vec{K}) \cdot \vec{\epsilon}_{\vec{k}\mu} V_{\vec{k}+\vec{K}} q_{\vec{k}} \rho_{\vec{K}+\vec{R}}^\dagger \\ - \sum_{\vec{k}_1, \vec{k}_2, \vec{k}_3} \frac{1}{2M} (\vec{k}_1 \cdot \vec{\epsilon}_{\vec{k}_2\mu_2}) (\vec{k}_1 \cdot \vec{\epsilon}_{\vec{k}_3\mu_3}) \\ \times V_{\vec{k}_1} q_{\vec{k}_2\mu_2} q_{\vec{k}_3\mu_3} \rho_{\vec{k}_1}^\dagger \Delta(\vec{k}_1 + \vec{k}_2 + \vec{k}_3). \quad (35)$$

Here $\vec{\epsilon}_{\vec{k}\mu}$ is the polarization vector of the phonon of wave vector \vec{k} and polarization index μ , and $\Delta(\vec{k}) \equiv \sum_{\vec{R}} \delta_{\vec{R}, \vec{R}+\vec{k}}$ is the pseudo- δ -function. Within the harmonic approximation the electron-ion contribution to the phonon dynamical matrix may be represented diagrammatically as shown in Fig. 1. The hatched circles correspond to correlation functions for the electrons including the effects both of the periodic ionic lattice and also of electron-electron interactions. The corresponding analytical expression for the electron-ion contribution to the dynamical matrix is

$$D_{ij}^{e-i} = \sum_{\vec{R}, \vec{R}'} n_I^2 (k_i + K_j) (k_j + K_i') V_{\vec{k}+\vec{R}} V_{\vec{k}+\vec{R}'} \bar{\chi}(\vec{k} + \vec{K}, -\vec{k} - \vec{K}') \\ - \sum_{\vec{R}} n_I K_i K_j V_{\vec{K}} \langle \rho_{\vec{K}}^\dagger \rangle. \quad (36)$$

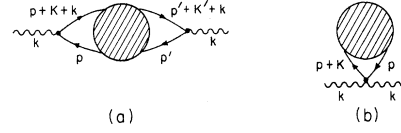


FIG. 1. Diagrams for the harmonic contribution to the dynamical matrix due to the electron-ion interaction. The hatched circles correspond to correlation functions for the electrons, including electron-electron interactions and electron-ion interactions.

Here $\bar{\chi}(\vec{k} + \vec{K}, -\vec{k} - \vec{K}')$ is the density-density correlation function for electrons moving in the periodic potential produced by the lattice. For the purpose of calculating phonon frequencies one may make the adiabatic approximation, and therefore electronic response functions may be evaluated at zero frequency. Also the effect of phonons on the motion of electrons gives rise to contributions to D of relative order $(m/M)^{1/2}$ and may be neglected, as has been shown by Migdal.^{11,22}

Let us now transform the second term in (36) to exhibit clearly the long-wavelength behavior. The expectation value of the electron density at a point \vec{x} is a functional of the potential acting on the electrons due to the presence of the periodic lattice; we denote this latter potential by $U(\vec{x}')$, and we make the dependence of ρ on U explicit by writing $\langle \rho(\vec{x}; [U(\vec{x}')]) \rangle$. If \vec{x} is increased by an amount \vec{a} and at the same time the static lattice potential is translated by the same amount, the electron density remains constant:

$$\langle \rho(\vec{x}; [U(\vec{x}')]) \rangle = \langle \rho(\vec{x} + \vec{a}; [U(\vec{x}' + \vec{a})]) \rangle. \quad (37)$$

Taking the gradient of Eq. (37) with respect to \vec{a} one finds

$$\nabla \langle \rho(\vec{x}) \rangle + \int d^3\vec{x}' \frac{\delta \langle \rho(\vec{x}) \rangle}{\delta U(\vec{x}')} \nabla U(\vec{x}') = 0, \quad (38)$$

or, on performing a Fourier transformation,

$$\vec{K} \langle \rho_{\vec{K}}^\dagger \rangle - n_I \sum_{\vec{K}'} \bar{\chi}(\vec{K}, -\vec{K}') \vec{K}' V_{\vec{K}'} = 0. \quad (39)$$

Substituting (39) into (36) one finds

$$D_{ij}^{e-i}(k) = \sum_{\vec{R}, \vec{R}'} [(k_i + K_j)(k_j + K_i') U_{\vec{k}+\vec{R}}^* U_{\vec{k}+\vec{R}'}^* \\ \times \bar{\chi}(\vec{k} + \vec{K}, -\vec{k} - \vec{K}') - K_i K_j' U_{\vec{K}} U_{\vec{K}'} \bar{\chi}(\vec{K}, -\vec{K}')] . \quad (40)$$

This result has also been derived by other authors.²³

In previous work it has been customary to replace $\bar{\chi}$ by its value for the electron gas in the presence of a uniform background of positive charge. However, as we shall show later, such calculations give results which, in the long-wavelength limit, are inconsistent with calculations of the elastic

constants based on second-order perturbation theory calculations of the energy of the system.

One way of taking into account the effect of the periodic ionic lattice on the motion of the electrons is to express $\bar{\chi}$ in terms of the propagator for electrons moving in a periodic potential. However, such a procedure entails performing a band-structure calculation, and is very cumbersome. In simple metals one expects band-structure effects on the electronic response functions to be small, and we therefore adopt an alternative procedure – we expand $\bar{\chi}$ in powers of the electron-ion interaction. Our study of the long-wavelength limit will show that the natural ordering parameter in the terms occurring in the expression for D_{ij} is not the total number of electron-ion interactions, but rather the total number of electron-ion umklapp processes – ones in which the total pseudo-wave-number changes by a reciprocal-lattice vector. In the discussion which follows we take into account all terms which contain no more than two umklapp processes; the appropriate diagrams in the expansion of D_{ij}^{e-i} are shown in Fig. 2.

The various graphs in Fig. 2 are correlated parts of the two-, three-, and four-point density correlation functions for the homogeneous electron gas. The analytical expressions which correspond to the diagrams shown in Fig. 2 are

$$k_i k_j U_k^2 \chi(k; \bar{\mu}) , \quad (41a)$$

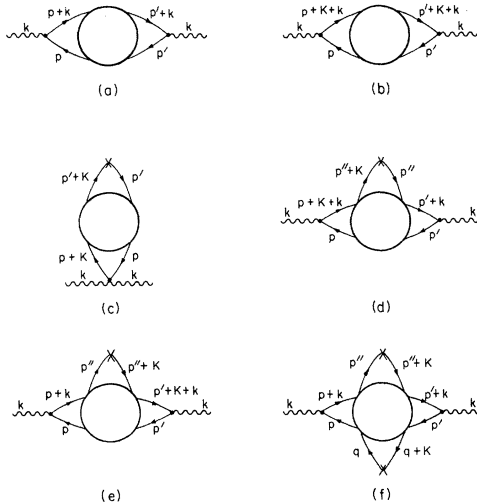


FIG. 2. Diagrams for the electron-ion contribution to the dynamical matrix. Only those diagrams containing no more than two electron-ion umklapp processes are shown. The circles represent connected parts (cumulants) of the two-, three-, and four-point density correlation functions for the homogeneous electron gas.

$$\sum_{\vec{K}}' (k_i + K_i)(k_j + K_j) U_{\vec{k}+\vec{K}}^2 \chi(\vec{k} + \vec{K}) , \quad (41b)$$

$$-\sum_{\vec{K}}' K_i K_j U_K^2 \chi(K) , \quad (41c)$$

$$\sum_{\vec{K}}' (k_i + K_i) k_j U_{\vec{k}+\vec{K}} U_k \chi(\vec{k} + \vec{K}, -\vec{K}, -\vec{k}) U_K , \quad (41d)$$

$$\sum_{\vec{K}}' k_i (k_j + K_j) U_k U_{\vec{k}+\vec{K}} \chi(\vec{k}, \vec{K}, -\vec{k} - \vec{K}) U_K , \quad (41e)$$

$$\frac{1}{2} \sum_{\vec{K}}' k_i k_j U_k^2 \chi(\vec{k}, \vec{K}, -\vec{K}, -\vec{k}) U_K^2 . \quad (41f)$$

In (41), $\chi(k)$ is the density-density correlation function for the homogeneous electron gas and the connected parts (cumulants) of the three- and four-point functions are denoted by $\chi(\vec{q}_1, \vec{q}_2, \vec{q}_3, \dots)$ where $\vec{q}_1, \vec{q}_2, \vec{q}_3, \dots$ are the momentum transfers at the external vertices. A prime on a sum over reciprocal-lattice vectors means that the null vector is to be excluded. We have also introduced the notation $U_k = n_I V_k$. In (41a) we have exhibited explicitly the dependence of χ on the chemical potential $\bar{\mu}$, since, as we shall see below, it is important to take into account the fact that the chemical potential of the electron gas is changed by the electron-ion interaction. Equation (41a) is the only term where the corrections to the chemical potential are important; in all other terms the effects are of higher order in the electron-ion interaction than the terms we are considering. The shift in the chemical potential $\bar{\mu} - \mu$ due to the electron-ion interaction may be found by calculating the energy of the electrons in the presence of the ionic lattice and then differentiating with respect to the electron density. To second order in the electron-ion interaction, the energy density of the electrons, measured with respect to the Hartree energy when the ions are distributed uniformly, is given by

$$\mathcal{E}_e = \mathcal{E}_e^{(0)} + \frac{1}{2} \sum_{\vec{K}} U_K^2 \chi(K) , \quad (42)$$

where $\mathcal{E}_e^{(0)}$ is the energy density of the electron gas in the presence of a uniform background of positive charge. By differentiating (42) with respect to the electron density n , one finds

$$\bar{\mu} - \mu = \frac{1}{2} \sum_{\vec{K}}' U_K^2 \frac{\partial \chi(K)}{\partial n} . \quad (43)$$

Thus to the required degree of accuracy we may write (41a) in the form

$$k_i k_j U_k^2 \chi(k; \bar{\mu}) = k_i k_j U_k^2 \chi(k; \mu) + k_i k_j U_k^2 \frac{\partial \chi(k)}{\partial \mu} \frac{1}{2} \sum_{\vec{K}}' U_K^2 \frac{\partial \chi(K)}{\partial \mu} \frac{d\mu}{dn} . \quad (44)$$

From now on in this section all correlation functions are to be evaluated with the chemical potential put equal to its value for the homogeneous electron gas. Adding (41b)–(41f), (44), and the ion-ion contribution D_{ij}^i , one finds the following expression for D_{ij} :

$$D_{ij}(k) = D_{ij}^0(\vec{k}) + k_i k_j U_k^2 \chi(k) + \frac{1}{2} k_i k_j U_k^2 \frac{\partial \chi(k)}{\partial \mu} \sum_{\vec{K}} U_K^2 \frac{\partial \chi(K)}{\partial \mu} \frac{d\mu}{dn} + \sum_{\vec{K}}' [(k_i + K_i)(k_j + K_j) U_{\vec{k}+\vec{K}}^2 \chi(\vec{k} + \vec{K}) - K_i K_j U_K^2 \chi(K)] \\ + \sum_{\vec{K}}' [(k_i + K_i)k_j + k_i(k_j + K_j)] U_{\vec{k}+\vec{K}} U_k \chi(\vec{k} + \vec{K}, -\vec{K}, -\vec{k}) U_K + \frac{1}{2} \sum_{\vec{K}}' k_i k_j U_k^2 \chi(\vec{k}, \vec{K}, -\vec{K}, -\vec{k}) U_K^2 \quad (45)$$

The ion-ion contribution may be written formally as follows:

$$D_{ij}^0 = k_i k_j n_I^2 \mathcal{V}_k + \sum_{\vec{K}}' n_I^2 [(k_i + K_i)(k_j + K_j) \mathcal{V}_{\vec{k}+\vec{K}} - K_i K_j \mathcal{V}_K], \quad (46)$$

where \mathcal{V}_k is the Fourier transform of the bare ion-ion interaction.

In previous calculations of phonon spectra the last two terms in (45) and the term due to the chemical potential shift have generally been neglected. The possible importance of such terms has been pointed out by Brovman and Kagan,²⁴ and numerical calculations which include these terms have been carried out by Johnson and Westin²⁵ and by Fehlner and the author²⁶, even for Na, K, and Al these terms have appreciable effects on the phonon frequencies. Next we consider the behavior of the dynamical matrix in the long-wavelength limit.

V. BEHAVIOR OF DYNAMICAL MATRIX AT LONG WAVELENGTH

The elastic constants may be determined from the long-wavelength limit of $D_{ij}(\vec{k})$ and it is instructive to compare these results with ones obtained from calculations of the energy of the uniform metal. As $k \rightarrow 0$ the bare electron-ion potential U_k behaves as $1/k^2$ whereas the various three- and four-point correlation functions behave as k^2 or k^4 .

To facilitate the discussion of the long-wavelength limit we introduce a screened electron-ion interaction and proper correlation functions. The screened electron-ion interaction is defined by the equation

$$\tilde{U}_k = U_k/\epsilon(k), \quad (47)$$

where

$$\epsilon(k) = \left(1 + \frac{4\pi e^2}{k^2} \chi(k)\right)^{-1} = 1 - \frac{4\pi e^2}{k^2} \chi_{sc}(k) \quad (48)$$

is the static dielectric function for the homogeneous electron gas. $\chi_{sc}(k)$ is the screened response function for the homogeneous electron gas. It is well known that in the long-wavelength limit²⁷

$$\lim_{k \rightarrow 0} \chi_{sc}(k) = -\frac{dn}{d\mu}. \quad (49)$$

The proper response functions are defined by the relations

$$\chi(\vec{q}_1, \vec{q}_2, \vec{q}_3) = \frac{\chi_{sc}(\vec{q}_2, \vec{q}_3; \vec{q}_1)}{\epsilon(q_1)} = \frac{\chi_{sc}(\vec{q}_1, \vec{q}_3; \vec{q}_2)}{\epsilon(q_2)} \\ = \frac{\chi_{sc}(\vec{q}_3; \vec{q}_1, \vec{q}_2)}{\epsilon(q_1)\epsilon(q_2)}, \quad \text{etc.} \quad (50)$$

The arguments of χ_{sc} to the right-hand side of the semicolon refer to the proper vertices.

On expanding Eq. (45) to second order in k , and using Eqs. (47), (48), and (50), one finds

$$D_{ij}(\vec{k}) = D_{ij}^0(\vec{k}) + k_i k_j \left[n^2 \frac{d\mu}{dn} - U_k^2 \frac{k^2}{4\pi e^2} + \sum_{\vec{K}}' U_K^2 \chi(K) + 2 \sum_{\vec{K}}' \frac{1}{3} K \frac{\partial}{\partial K} [U_K^2 \chi(K)] + \sum_{\vec{K}}' K_l^2 K_m^2 K \frac{\partial}{\partial K} \frac{1}{K} \frac{\partial}{\partial K} [U_K^2 \chi(K)] \right. \\ - 2n \frac{d\mu}{dn} \sum_{\vec{K}}' [U_K^2 \chi_{sc}(\vec{K}, -\vec{K}; 0) + \frac{1}{3} U_K \vec{K} \cdot \vec{\nabla}_{\vec{k}} (U_{\vec{k}+\vec{K}} \chi_{sc}(\vec{k} + \vec{K}, -\vec{K}, -\vec{k}))|_{k=0}] + \frac{1}{2} n^2 \left(\frac{d\mu}{dn} \right)^2 \sum_{\vec{K}}' U_K^2 \frac{\partial^2 \chi(K)}{\partial \mu^2} \\ + \frac{1}{2} n^2 \frac{d^2 \mu}{dn^2} \sum_{\vec{K}}' U_K^2 \frac{\partial \chi(K)}{\partial \mu} \left. \right] + k_i^2 \delta_{ij} \sum_{\vec{K}}' \left(\frac{1}{3} K^4 - 5K_l^2 K_m^2 \right) \frac{1}{2K} \frac{\partial}{\partial K} \frac{1}{K} \frac{\partial}{\partial K} [U_K^2 \chi(K)] \\ + k^2 \delta_{ij} \sum_{\vec{K}}' \left(K_l^2 K_m^2 \frac{1}{2K} \frac{\partial}{\partial K} \frac{1}{K} \frac{\partial}{\partial K} [U_K^2 \chi(K)] + \frac{1}{6} K \frac{\partial}{\partial K} [U_K^2 \chi(K)] \right) \quad (51)$$

The indices l and m refer to two different cubic axes of the system. Equation (51) may be further simplified by using the following identities discussed in the Appendix:

$$\chi_{sc}(\vec{K}, -\vec{K}; 0) = -\frac{\partial}{\partial \mu} \chi(K), \quad (52)$$

$$\lim_{k \rightarrow 0} \chi_{sc}(\vec{K}, -\vec{K}; \vec{k}, -\vec{k}) = \frac{\partial^2 \chi(K)}{\partial \mu^2}, \quad (53)$$

$$\vec{K} \cdot \vec{\nabla}_{\vec{k}} \chi_{sc}(\vec{k} + \vec{K}, -\vec{K}; -\vec{k}) = \frac{1}{2} K \frac{\partial^2}{\partial K \partial \mu} \chi(K). \quad (54)$$

Substituting Eqs. (52)–(54) into Eq. (51) we find

$$\begin{aligned}
D_{ij}(\vec{k}) = & D_{ij}^0(k) + k_i k_j \left\{ -U_k^2 \frac{k^2}{4\pi e^2} + n^2 \frac{d\mu}{dn} + \sum_{\vec{K}}' U_K^2 \chi(K) + 2 \sum_{\vec{K}}' \frac{1}{3} K \frac{\partial}{\partial K} U_K^2 \chi(K) \right. \\
& + 2 \sum_{\vec{K}}' \frac{K_i^2 K_m^2}{K^4} \left[\frac{1}{2} \left(K \frac{\partial}{\partial K} \right)^2 U_K^2 \chi(K) - K \frac{\partial}{\partial K} U_K^2 \chi(K) \right] + 2n \sum_{\vec{K}}' \left(U_K^2 \frac{\partial \chi(K)}{\partial n} + \frac{1}{6} K \frac{\partial}{\partial K} U_K^2 \frac{\partial \chi(K)}{\partial n} \right) \\
& + \frac{1}{2} n^2 \sum_{\vec{K}}' U_K^2 \frac{\partial^2 \chi(K)}{\partial n^2} \left. \right\} + k_i^2 \delta_{ij} \sum_{\vec{K}}' \left(\frac{1}{3} - \frac{5K_i^2 K_m^2}{K^4} \right) \left[\frac{1}{2} \left(K \frac{\partial}{\partial K} \right)^2 U_K^2 \chi(K) - K \frac{\partial}{\partial K} U_K^2 \chi(K) \right] \\
& + k^2 \delta_{ij} \sum_{\vec{K}}' \left\{ \left(\frac{K_i^2 K_m^2}{K^4} \right) \left[\frac{1}{2} \left(K \frac{\partial}{\partial K} \right)^2 U_K^2 \chi(K) - K \frac{\partial}{\partial K} U_K^2 \chi(K) \right] + \left(\frac{1}{6} K \frac{\partial}{\partial K} U_K^2 \chi(K) \right) \right\} . \quad (55)
\end{aligned}$$

The long-wavelength dynamical matrix for a cubic material may be expressed in terms of the elastic constants by means of the relation

$$D_{ij}(\vec{k}) = (C_{12} + C_{44})k_i k_j + (C_{11} - C_{12} - 2C_{44})k_i^2 \delta_{ij} + C_{44}k^2 \delta_{ij} . \quad (56)$$

Comparing Eqs. (55) and (56) and using Eq. (46) for D_{ij}^0 , one finds for the bulk modulus

$$\begin{aligned}
B = \frac{1}{3}(C_{11} + 2C_{12}) = & \lim_{k \rightarrow 0} \left(n_I^2 \mathcal{V}_k - U_k^2 \frac{k^2}{4\pi e^2} \right) + n^2 \frac{d\mu}{dn} + \sum_{\vec{K}}' \left[1 + \frac{1}{2} \left(K \frac{\partial}{\partial K} \right) + \frac{1}{18} \left(K \frac{\partial}{\partial K} \right)^2 \right] [n_I^2 \mathcal{V}_K + U_K^2 \chi(K)] \\
& + 2n \sum_{\vec{K}}' U_K^2 \frac{\partial \chi(K)}{\partial n} + n \sum_{\vec{K}}' \frac{1}{3} K \frac{\partial}{\partial K} U_K^2 \frac{\partial \chi(K)}{\partial n} + \frac{1}{2} n^2 \sum_{\vec{K}}' U_K^2 \frac{\partial^2 \chi(K)}{\partial n^2} . \quad (57)
\end{aligned}$$

The bulk modulus may also be determined from the change in the energy of the electron-ion system under uniform compression. To second order in the electron-ion interaction the energy density is given by²⁸

$$\begin{aligned}
\mathcal{E}(n) = & \frac{1}{2} n^2 \lim_{k \rightarrow 0} \left(\frac{\mathcal{V}_k}{Z^2} + \frac{4\pi e^2}{k^2} + \frac{2\mathcal{V}_k}{Z} \right) \\
& + \left(\frac{1}{2} n_I^2 \sum_{\vec{K}}' \mathcal{V}_K - n_I \mathcal{V}(r=0) \right) + \mathcal{E}_e^{(0)}(n) + \frac{1}{2} \sum_{\vec{K}}' U_K^2 \chi(K) \quad (58)
\end{aligned}$$

The first term in (58) is the long-wavelength contribution to the Hartree energy, the second term is a formal expression for the Madelung energy [$\mathcal{V}(r=0)$ is the electron-ion potential for zero spatial separation], the third term is the energy density of the homogeneous electron gas, and the final term is the correction to the energy due to the periodic part of the electron-ion interaction (the band-structure energy). B is given by $n^2 d^2 \mathcal{E}(n)/dn^2$, and using Eq. (58) for $\mathcal{E}(n)$ one obtains Eq. (57) for B . Thus the calculations of B from the phonon dynamical matrix and from the second-order perturbation theory expression for the energy are consistent with each other.

Expressions for the other elastic constants may be obtained from Eqs. (55) and (56); the results are

$$C_{11} + 2C_{44} = \frac{1}{3}(C_{44} + 2C_{12}) + \sum_{\vec{K}}' \left[\left(\frac{1}{3} K \frac{\partial}{\partial K} \right)^2 + \frac{1}{3} K \frac{\partial}{\partial K} \right]$$

$$\times [U_K^2 \chi(K) + n_I^2 \mathcal{V}_K] , \quad (59)$$

$$\begin{aligned}
C_{44} = & \sum_{\vec{K}}' \left\{ \frac{K_i^2 K_m^2}{K^4} \left[\frac{1}{2} \left(K \frac{\partial}{\partial K} \right)^2 - K \frac{\partial}{\partial K} \right] [U_K^2 \chi(K) + n_I^2 \mathcal{V}_K] \right. \\
& \left. + \frac{1}{6} K \frac{\partial}{\partial K} [U_K^2 \chi(K) + n_I^2 \mathcal{V}_K] \right\} . \quad (60)
\end{aligned}$$

The important conclusion of this work is that one must include in calculations of the dynamical matrix terms of third and fourth order in the electron-ion interaction if results are to be consistent with calculations of the elastic constants based on the second-order perturbation expression for the energy. The reason for this is not difficult to see: It is that the long-wavelength screened electron-ion interaction depends only on electronic response functions and is independent of the details of the bare electron-ion interaction; consequently some terms in D of third and fourth order in the electron-ion interaction reduce to second-order terms in the long-wavelength limit. The only electron-ion interactions which appear explicitly in the long-wavelength limit are ones which involve umklapp processes.

As we noted above, in the long-wavelength limit the screened electron-ion interaction \tilde{U}_k tends to $-n d\mu/dn$. Such energies are comparable to typical excitation energies of the homogeneous electron system, and consequently long-wavelength components of the electron-ion interaction cannot be

treated as a small perturbation. However, the electron-ion interaction at an umklapp process always corresponds to a wave number lying outside the first Brillouin zone, and the magnitude of the screened interaction for such a process will be considerably less than $n d\mu/dn$. Thus, at least for long-wavelength phonons, the total number of umklapp processes is a useful parameter for ordering contributions to the dynamical matrix. For wave numbers near the boundary of the first Brillouin zone the situation is less clear; \bar{U}_k is then comparable to the screened interaction for some umklapp processes, and therefore the total number of electron-ion interactions will probably be a better ordering parameter.

The fact that second-order perturbation theory calculations of the dynamical matrix are inconsistent with calculations of the elastic constants based on second-order perturbation theory calculations of the energy of the uniform metal has previously been pointed out by Wallace,²⁹ who evaluated the magnitude of the difference between the two expressions for the elastic constants for a number of simple metals. In the above calculations we have to obtain consistency between the two ways of calculating the elastic constants.

VI. DISCUSSION OF RESULTS FOR PHONON DYNAMICAL MATRIX

Let us first consider the expression for the bulk modulus, Eq. (57). The first term is the difference between two divergent quantities and results from the dependence of the energy of the bottom of the conduction band on the volume of the system. The second term is the bulk modulus of the electrons in the absence of the periodic lattice and the final term is a correction to the bulk modulus of the electrons due to the periodic lattice. The third term in (57) is the contribution from the bare ion-ion interaction \mathcal{V}_k , as well as a contribution from what may be regarded as an electron-induced ion-ion potential $V_k^2 \chi(k)$. The remaining terms come from the density dependence of $\chi(K)$; neither these terms nor the corrections to the bulk modulus of the electrons would appear if contributions (41d)–(41f) were omitted in the calculation for the dynamical matrix.

As has previously been pointed out,^{6,20} if the terms (41d)–(41f) are omitted, D_{ij} is given by the same expression as D_{ij}^0 [Eq. (46)] but with the bare ion-ion potential \mathcal{V}_k replaced by an effective ion-ion potential $\mathcal{V}_k + V_k^2 \chi(k)$. In other words in this approximation the electron-ion interaction gives rise to an additional force which acts only between pairs of ions and which depends only on the separation of the ions. When (41d)–(41f) are included in the calculation the effect of the electron-ion interaction is not so simple – the force between two ions depends

not only on the separation of the ions but also on the position of the two ions relative to the other ions in the system.

Next we return again to the long-wavelength limit to show how the low-order perturbation calculation above is related to more general results. As one can see from Eq. (36), the contribution to $D_{ij}^{\alpha\beta}(\vec{k})$ which does not involve umklapp processes at the electron-phonon vertices is given in general by

$$n_i^2 k_i k_j V_k^2 \bar{\chi}(\vec{k}, \vec{k}) . \quad (61)$$

Just as in our earlier discussion of the transverse response of electrons moving in a periodic lattice, one can define a dielectric function $\bar{\epsilon}(\vec{k})$ which is given by the ratio of the applied electrostatic field of wave number \vec{k} to the total electric field at the same wave number, the ratio being evaluated when the only component of the external field has wave number \vec{k} . This dielectric function is given by

$$[\bar{\epsilon}(\vec{k})]^{-1} = 1 + (4\pi e^2/k^2) \bar{\chi}(\vec{k}, \vec{k}) . \quad (62)$$

One can also define a screened response function $\bar{\chi}_{sc}(\vec{k})$ given by

$$\bar{\chi}_{sc}(\vec{k}) = \bar{\chi}(\vec{k}, \vec{k}) \bar{\epsilon}(\vec{k}) . \quad (63)$$

$\bar{\chi}_{sc}(\vec{k})$ consists of all contributions to $\bar{\chi}(\vec{k}, \vec{k})$ which do not involve a polarization process of momentum \vec{k} . As we show in the Appendix,

$$\lim_{k \rightarrow 0} \bar{\chi}_{sc}(\vec{k}) = - \frac{dn}{d\mu} . \quad (64)$$

Thus in the long-wavelength limit we may write

$$k_i k_j U_k^2 \bar{\chi}(\vec{k}, \vec{k}) = - k_i k_j U_k^2 \frac{k^2}{4\pi e^2} + k_i k_j \frac{d\bar{\mu}}{dn} \left[1 + O\left(\frac{k^2}{k_F^2}\right) \right] . \quad (65)$$

If in the calculation of the bulk modulus we had used the full expression for $\bar{\chi}(\vec{k}, \vec{k})$ instead of an approximate expression, the terms

$$n^2 \frac{d\mu}{dn} + \frac{1}{2} n^2 \sum_{\vec{K}} U_K^2 \frac{\partial^2 \chi(K)}{\partial n^2}$$

in (57) would have been replaced by $n^2 d\bar{\mu}/dn$. In fact,

$$\frac{d\mu}{dn} + \frac{1}{2} \sum_{\vec{K}} U_K^2 \frac{\partial^2 \chi(K)}{\partial n^2}$$

is $d\bar{\mu}/dn$ calculated to second order in the electron-ion interaction.

The compressibility κ of the electron system \bar{s}_- is given by

$$\frac{1}{\kappa} = n^2 \frac{d\bar{\mu}}{dn} . \quad (66)$$

If one defines a macroscopic sound velocity \bar{s}_- for the electrons \bar{s}_- by the relation

$$m\bar{s}_i^2 = n \frac{d\bar{\mu}}{dn} = \frac{1}{n\kappa}, \quad (67)$$

the contribution to D_{ij}^{0-i} may be written as

$$n\bar{s}_{k_i k_j}^2, \quad (68)$$

which is an obvious generalization of a result of Pines³⁰ to the case of electrons moving in a periodic potential. It should be noted that in (66) the variation of the electron density is to be performed leaving the configuration of the lattice unaltered. Our discussion could have been couched in terms of diagrammatic techniques and Ward identities, as stated by Heine, Nozières, and Wilkins,¹⁶ but we prefer to exhibit the physical meaning of the results by deriving them from macroscopic considerations.

It is instructive to examine in a little detail the origin of the term

$$\frac{1}{2}n^2 \sum_K' U_K^2 \frac{\partial^2 \chi(K)}{\partial^2 n}$$

which occurs in (57). In the calculation of the bulk modulus from the dynamical matrix it arose from two contributions – the correction to the chemical potential in (41a), and from (41f). The latter term describes the effect of the scattering of electrons from the lattice, the chemical potential of the electrons being held fixed; if all possible scatterings of electrons from the periodic lattice were taken into account the result would be equivalent to replacing all the plane-wave electron propagators in the expression for $\chi(k)$ by Bloch wave propagators. If the chemical potential is held constant, the density of electrons in the presence of the ionic lattice will generally be different from its value in the homogeneous electron gas. The change in the chemical potential ensures that the density of electrons remains constant.

VII. CONCLUSION

Most calculations of properties of metals entail rather lengthy calculations, and it is frequently difficult to know which particular assumption is responsible for any discrepancy between theory and experiment. Is it due to many-body effects, to the inadequacy of the bare electron-ion interaction used, or to the use of low-order perturbation theory in calculating the effects of the electron-ion interaction? The work described above may be used to provide a partial answer to this question since it shows how, within the framework of a local, energy-independent pseudopotential model, one may take into account electron-ion interactions and many-body effects. The identities derived in the Appendix also provide a consistency check on approximations for the correlation functions for the homogeneous electron gas.

A number of extensions of the above work may be easily carried out. First, higher-order electron-ion interactions can be included, and second, the effects of anharmonicity can be included in the phonon calculations. A third less straightforward extension is to the case of nonlocal and energy-dependent pseudopotentials. One way to proceed is formally to calculate quantities in terms of Bloch wave states for the electrons, and then to expand the Bloch wave propagators in a plane-wave basis.²¹ Another method, closely related to the orthogonalized-plane-wave (OPW) method for calculating single-electron states, has been described by Basani, Robinson, Goodman, and Schrieffer.³¹ In both these methods one has to exercise caution in estimating the magnitude of terms, since projection operators which appear in the formalisms have the property that $P^2 = P$; in other words the ordering of terms in a perturbation expansion is ambiguous.

Note added in proof. A discussion similar to our own of the long-wavelength phonon spectrum has recently been given by E. G. Brovman and Yu. Kagan, *Zh. Eksperim. i Teor. Fiz.* **57**, 1327 (1969) [*Soviet Phys. JETP* **30**, 721 (1970)], and E. G. Brovman, Yu. Kagan, and A. Kholas, *Zh. Eksperim. i Teor. Fiz.* **57**, 1635 (1969) [*Soviet Phys. JETP* **30**, 883 (1970)].

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APPENDIX

Here we derive a number of long-wavelength properties of response functions. First, we consider $\bar{\chi}(\vec{k}, -\vec{k})$. If a weak external potential $\delta U_{\vec{k}}$ is applied to a system of electrons moving in a periodic lattice, the response of the system at wave number \vec{k} is given by

$$\delta\langle\rho_{\vec{k}}\rangle = \bar{\chi}(\vec{k}, -\vec{k})\delta U_{\vec{k}} \quad (A1)$$

$$= \bar{\chi}_{sc}(\vec{k})\delta U_{\vec{k}}/\bar{\epsilon}(\vec{k}) \quad (A2)$$

$$= \bar{\chi}_{sc}(\vec{k})\delta\bar{U}_{\vec{k}}, \quad (A3)$$

where $\delta\bar{U}_{\vec{k}}$ is the screened potential and $\bar{\chi}_{sc}$ and $\bar{\epsilon}$ are defined in Eqs. (62) and (63). Now in the long-wavelength limit, equilibrium will be reached when the sum of the local chemical potential $\bar{\mu}(\vec{r})$ and the local screened potential are constant; that is,

$$\bar{\mu}(\vec{r}) + \bar{U}(\vec{r}) = \text{const.} \quad (A4)$$

Thus, using (A3) and (A4) we may write

$$\lim_{k \rightarrow 0} \bar{\chi}_{sc}(\vec{k}) = \lim_{k \rightarrow 0} \frac{\delta \langle \rho_{\vec{k}} \rangle}{\delta \bar{U}_{\vec{k}}} = \frac{dn}{d\bar{U}} = -\frac{dn}{d\bar{\mu}}, \quad (\text{A5})$$

which is the first of the required identities.

The remaining identities are for response functions for the homogeneous electron gas. The first two of these are

$$\chi_{sc}(\vec{K}, -\vec{K}; 0) = -\frac{\partial \chi(K)}{\partial \bar{\mu}}, \quad (\text{A6})$$

$$\lim_{k \rightarrow 0} \chi_{sc}(\vec{K}, -\vec{K}; \vec{k}, -\vec{k}) = \frac{\partial^2 \chi(K)}{\partial \bar{\mu}^2}. \quad (\text{A7})$$

One way of proving these identities is to use diagrammatic methods. The operator $\partial/\partial\bar{\mu}$ acting on an electron propagator generates a density vertex carrying zero frequency and whose wave number tends to zero. Moreover, since the zero-wave-number Hartree terms have been eliminated from the calculation of properties of the homogeneous electron gas, the vertex generated by $\partial/\partial\bar{\mu}$ is proper.

A second approach has a more physical interpretation. $\chi_{sc}(\vec{K}, -\vec{K}; 0)$ is the linear response of $\chi(K)$ to a long-wavelength screened field $\delta\bar{U}(\vec{r})$. Now, as we mentioned above [cf. (A4)], equilibrium will be established when

$$\delta\mu(\vec{r}) + \delta\bar{U}(\vec{r}) = 0, \quad (\text{A8})$$

from which it follows immediately that

$$\chi_{sc}(K, -K; 0) = \frac{\delta \chi(K)}{\delta \bar{U}} = -\frac{\partial \chi(K)}{\partial \bar{\mu}}, \quad (\text{A9})$$

which is Eq. (A6). Equation (A7) follows from (A6) by a second application of $\partial/\partial\bar{\mu}$.

The third identity is

$$2\vec{K} \cdot \vec{\nabla}_{\vec{k}} \chi(\vec{k} + \vec{K}, -\vec{K}; -\vec{k}) = K \frac{\partial^2 \chi(K)}{\partial K \partial \bar{\mu}}. \quad (\text{A10})$$

To prove this we first observe that

$$\frac{\partial^2 \chi(K)}{\partial K \partial \bar{\mu}} = -\frac{\partial}{\partial K} \chi(\vec{K}, -\vec{K}; 0), \quad (\text{A11})$$

which follows from Eq. (A6). Consider now the quantity $\chi_{sc}(\vec{K} + \vec{k}, -\vec{K} - \vec{k}; 0) - \chi_{sc}(\vec{K}, -\vec{K}; 0)$, which we write in the following way:

$$\begin{aligned} & \chi_{sc}(\vec{K} + \vec{k}, -\vec{K} - \vec{k}; 0) - \chi_{sc}(\vec{K}, -\vec{K}; 0) \\ &= \chi_{sc}(\vec{K} + \vec{k}, -\vec{K} - \vec{k}; 0) - \chi_{sc}(\vec{K} + \vec{k}, -\vec{K}; -\vec{k}) \\ &+ \chi_{sc}(\vec{K} + \vec{k}, -\vec{K}; -\vec{k}) - \chi_{sc}(\vec{K}, -\vec{K}; 0) \\ &= 2[\chi_{sc}(\vec{K} + \vec{k}, -\vec{K}; -\vec{k}) - \chi_{sc}(\vec{K}, -\vec{K}; 0)] \left[1 + O\left(\frac{k}{K}\right) \right]. \end{aligned} \quad (\text{A12})$$

In deriving (A12) we used the invariance of the response function under the parity transformation. Equation (A10) follows immediately from (A11) and (A12).

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PHYSICAL REVIEW B

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Theory of the Diamagnetic Interactions among the Conduction Electrons in Metals*

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The thermodynamic potential of a metal in the presence of a weakly nonuniform magnetic field of induction $B(\mathbf{r})$ is evaluated. The calculation is a mean-field theory for the interaction between the magnetization at different points in the metal, and is restricted to magnetic field strengths for which the Fermi energy is large compared to the separation between Landau levels. An integral equation for the spatially varying part of the magnetic induction is obtained by minimizing the appropriate thermodynamic potential of the system. The solution of this integral equation is studied. Both domain-type and magnetization-density-wave solutions can be obtained for appropriate Fermi surfaces. The nature of each of these solutions as discussed.

I. INTRODUCTION

There has been considerable interest recently in the effect of the magnetic interactions among the conduction electrons on diamagnetism in metals. This problem first arose with the study by Shoenberg¹ of the wave shape of de Haas-van Alphen oscillations in silver. Shoenberg suggested that the magnetization M of the real metal as a function of the magnetic field strength H could be approximated by the magnetization of a system of noninteracting electrons in the presence of the field $\vec{B} = \vec{H} + 4\pi\vec{M}$. This conjecture agrees with a simple self-consistent-field calculation of the magnetization.² Pippard³ showed that this prescription for determining the magnetization could lead to a multiple-valued function $M(H)$, and he investigated the thermodynamic behavior of the system as a function of H . He found that the path of minimum free energy led to an abrupt jump in the magnetization in the region where $M(H)$ is multiple valued. In Pippard's work, the sample was implicitly assumed to be a long thin rod oriented parallel to the applied magnetic field. A very interesting situation, first pointed out by Condon,⁴ arises when the sample has a finite demagnetizing factor. In that case, there can exist a region of applied magnetic field strength in which no portion of the H - B isotherm is thermodynamically stable. As shown

by Condon, the sample must in this case spontaneously divide into regions with different values of the magnetization, and a domain structure results. The domains are regions in which the magnetization is uniform; in the domain walls the magnetization changes smoothly from its value in one domain to its value in the neighboring domain. The behavior of the system is analogous to the condensation of a gas, with the two different states of magnetization playing the roles of the liquid and gas phases.

Another interesting possibility, the magnetization-density-wave (MDW) state was first suggested by the study of the wave-number-dependent susceptibility⁵ $\chi(q)$. If we define $\chi(q) = dM(q)/dB(q)$, then the wave-number-dependent permeability $\mu(q) = dB(q)/dH(q)$ is equal to $[1 - 4\pi\chi(q)]^{-1}$. When $4\pi\chi(q)$ becomes equal to unity, $\mu(q)$ diverges. This implies that the system is capable of sustaining a nonvanishing spatially varying magnetic induction dB_q without any driving force dH_q . For the free-electron model⁶ $\chi(q)$ is given by

$$(\partial M_0 / \partial B_0) [2J_1(qr_c) / qr_c]^2,$$

where M_0 and B_0 are the spatially uniform magnetization and induction and r_c is the cyclotron radius of the extremal orbit on the Fermi surface. $J_1(x)$ is the Bessel function of order unity. In