

Surface Excitations in the Random-Phase Approximation. II. Retardation Effects*

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Within the framework of a linear-response correlation-function approach to the collective modes in an inhomogeneous electron gas, a theory is given of the effect of retardation on surface plasmons. The case of a sharp metal-vacuum interface is worked out in detail as an illustration of the general formalism.

I. INTRODUCTION

It is well known that the electromagnetic fields which are produced by charge fluctuations give rise to a strong modification of the surface-plasmon dispersion relation at long wavelengths. The simple case of a sharp metal-vacuum plane interface is amenable to an elementary treatment (see, for example, Economu¹). It is found that for $q < \omega_p/c$, the surface plasmon is simply a transverse photon. Here q is the wave vector, c is the speed of light, and ω_p is the bulk-plasma frequency.

Fedders² and Feibelman³ have discussed the problem of surface plasmons in the electrostatic approximation ($c \rightarrow \infty$) using the concepts and techniques of many-body theory [in the random-phase approximation (RPA)]. This kind of formulation is necessary if one wishes, for example, to deal with a smoothly varying electronic density in the interface region or to include the effects of lattice structure in a fundamental way. The authors have recently⁴ given a many-body formulation of surface problems based on linear-response theory and the equation of motion for the Wigner distribution function. We believe that our approach brings out the common features of collective modes in many-body systems, be they homogeneous or inhomogeneous. In this paper, we extend our earlier discussion to include retardation effects. We believe that this is the first time that such effects have been discussed within the framework of a linear-response correlation-function approach.

After the magnetic field is eliminated from Maxwell's equations, we have

$$\begin{aligned} \vec{\nabla} \times \vec{\nabla} \times \delta \vec{E} &= -\frac{1}{c} \frac{\partial}{\partial t} \left[\frac{4\pi}{c} \delta \vec{J} + \frac{1}{c} \frac{\partial \delta \vec{E}}{\partial t} \right], \\ \vec{\nabla} \cdot \delta \vec{E} &= 4\pi \delta \rho, \quad \frac{\partial}{\partial t} \delta \rho + \vec{\nabla} \cdot \delta \vec{J} = 0. \end{aligned} \quad (1.1)$$

These give the local electric field fluctuations in terms of the local electromagnetic current ($\delta \vec{J}$) and charge ($\delta \rho$) densities. Fourier transforming into (\vec{k}, ω) space, we may combine the equations in (1.1) to give ($i = x, y, z$)

$$\delta E_i(\vec{k}, \omega) = -\frac{4\pi i}{\omega(\omega^2 - c^2 k^2)} \sum_j (\omega^2 \delta_{ij} - c^2 k_i k_j) \delta J_j(\vec{k}, \omega). \quad (1.2)$$

Assuming a weak external time-dependent electric field, we have a linear constitutive relation between the local current and the local (effective) electric field,

$$\delta J_i(\vec{k}, \omega) = \sum_j \int \frac{d\vec{p}}{(2\pi)^3} \bar{\sigma}_{ij}(\vec{k}, -\vec{p}, \omega) \delta E_j(\vec{p}, \omega). \quad (1.3)$$

We shall refer to $\bar{\sigma}_{ij}$ as the screened or local conductivity. Inserting (1.3) into (1.2), we have the following coupled-integral equation which the components of the local electric field must satisfy:

$$\begin{aligned} \delta E_i(\vec{k}, \omega) &= -\frac{4\pi i}{\omega(\omega^2 - c^2 k^2)} \sum_{j,1} \int \frac{d\vec{p}}{(2\pi)^3} (\omega^2 \delta_{ij} - c^2 k_i k_j) \\ &\quad \times \bar{\sigma}_{ji}(\vec{k}, -\vec{p}, \omega) \delta E_1(\vec{p}, \omega). \end{aligned} \quad (1.4)$$

This equation will determine the dispersion relation of both bulk and surface collective oscillations.

In this generalized dielectric formulation,^{5,6} the question of surface plasmons is reduced to the problem of finding the components of the local conductivity $\bar{\sigma}_{ij}(\vec{k}, -\vec{p}, \omega)$. In Sec. II and the Appendix, we show how to determine this quantity within the RPA by using an equation of motion for the Wigner distribution function in the presence of external time-dependent fields. To leading order in ω^{-1} (high-frequency limit), only the diamagnetic current contributes, and we find simply

$$\bar{\sigma}_{ij}(\vec{k}, -\vec{p}, \omega) = \frac{ie^2}{m\omega} n_0(\vec{k} - \vec{p}) \delta_{ij} + O\left(\frac{1}{\omega^3}\right), \quad (1.5)$$

where $n_0(\vec{k})$ is the Fourier transform of the static density distribution. In Sec. III we briefly discuss the nontrivial solutions of (1.4) using (1.5). In particular, we show that in the electrostatic limit, the results of Ref. 4 are recovered. As an illustration of retardation effects, we then compute the surface-plasmon dispersion relation for the simple case of a sharp metal-vacuum interface.

The results are well known from more elementary wave-matching calculations.¹ However, the latter method cannot be generalized to deal with realistic density profiles. Our approach provides a general framework within which the significance of special limiting cases can be judged.

II. LOCAL CONDUCTIVITY OF INHOMOGENEOUS ELECTRON GAS

The interaction of a weak external electromagnetic field with a gas of electrons is given by the standard expression

$$V = e \int d\vec{r} n(\vec{r}) \phi^{\text{ext}}(\vec{r}, t) - (e/c) \int d\vec{r} \vec{j}(\vec{r}) \cdot \vec{A}^{\text{ext}}(\vec{r}, t), \quad (2.1)$$

where e is the actual charge of an electron (< 0) and, in terms of the electronic field operators, the particle density and current operators are

$$n(\vec{r}) = \psi^\dagger(\vec{r})\psi(\vec{r}), \quad (2.2)$$

$$\vec{j}(\vec{r}) = \frac{\hbar}{2mi} (\vec{\nabla}_r - \vec{\nabla}_{r'}) \psi^\dagger(\vec{r})\psi(\vec{r}') \Big|_{\vec{r}=\vec{r}'}$$

The potentials (ϕ, \vec{A}) are c numbers. Using linear-response theory, one finds that the perturbation (2.1) induces an electric current given by

$$\begin{aligned} \delta \vec{J}(\vec{k}, \omega) = & -\frac{e^2}{mc} \int \frac{d\vec{p}}{(2\pi)^3} n_0(\vec{k} - \vec{p}) \vec{A}^{\text{ext}}(\vec{p}, \omega) \\ & - e^2 \int \frac{d\vec{p}}{(2\pi)^3} \chi_{j_n}(\vec{k}, -\vec{p}, \omega) \phi^{\text{ext}}(\vec{p}, \omega) \\ & + \frac{e^2}{c} \int \frac{d\vec{p}}{(2\pi)^3} \chi_{j_j}(\vec{k}, -\vec{p}, \omega) \cdot \vec{A}^{\text{ext}}(\vec{p}, \omega). \end{aligned} \quad (2.3)$$

The first term on the right-hand side is the so-called diamagnetic current. The current-current correlation function is defined as follows:

$$\chi_{j_j}(\vec{k}, \vec{p}, \omega) = \int_{-\infty}^{\infty} \frac{d\omega'}{2\pi} \frac{\chi_{j_j}''(\vec{k}, \vec{p}, \omega')}{\omega' - \omega - i0^+}, \quad (2.4)$$

with

$$\begin{aligned} \chi_{j_j}''(\vec{k}, \vec{p}, \omega) \equiv & \int_{-\infty}^{\infty} dt \int d\vec{r} \int d\vec{r}' e^{-i\vec{k}\cdot\vec{r} - i\vec{p}\cdot\vec{r}'} e^{i\omega t} \\ & \times i \langle [\vec{j}(\vec{r}, t), \vec{j}(\vec{r}', 0)] \rangle_0 \\ & = \int_{-\infty}^{\infty} dt e^{i\omega t} i \langle [\vec{j}(\vec{k}, t), \vec{j}(\vec{p}, 0)] \rangle_0, \end{aligned} \quad (2.5)$$

where the average is over the unperturbed Hamiltonian and $\vec{j}(t)$ is in the Heisenberg representation. The current-density correlation function $\chi_{j_n}(\vec{k}, \vec{p}, \omega)$ is defined in an equivalent fashion.

As is well known,⁶ the requirement that the induced electrical current be invariant under an arbitrary gauge transformation

$$\phi'(\vec{r}, t) = \phi(\vec{r}, t) + \frac{1}{c} \frac{\partial}{\partial t} \Lambda(\vec{r}, t), \quad (2.6)$$

$$\vec{A}'(\vec{r}, t) = \vec{A}(\vec{r}, t) - \vec{\nabla} \Lambda(\vec{r}, t)$$

implies that

$$\left(\chi_{j_j}(\vec{k}, -\vec{p}, \omega) \cdot -\frac{n_0(\vec{k} - \vec{p})}{m} \right) \vec{p} = \omega \chi_{j_n}(\vec{k}, -\vec{p}, \omega). \quad (2.7)$$

In the first term on the left-hand side of (2.7), the multiplication involves a dot product of \vec{p} with $\vec{j}(-\vec{p})$ in the correlation function defined by (2.5). Assuming that our approximate calculations are consistent with (2.7), we may simplify (2.3) to

$$\begin{aligned} \delta \vec{J}(\vec{k}, \omega) = & \frac{e^2}{i\omega} \int \frac{d\vec{p}}{(2\pi)^3} \left(\chi_{j_j}(\vec{k}, -\vec{p}, \omega) \cdot -\frac{n_0(\vec{k} - \vec{p})}{m} \right) \\ & \times \delta \vec{E}^{\text{ext}}(\vec{p}, \omega), \end{aligned} \quad (2.8)$$

where the external electric field is given by

$$\delta \vec{E}^{\text{ext}}(\vec{p}, \omega) \equiv -i \vec{p} \phi^{\text{ext}}(\vec{p}, \omega) + (i\omega/c) \vec{A}^{\text{ext}}(\vec{p}, \omega). \quad (2.9)$$

Equation (2.8) may be written in a form analogous to (1.3), the true conductivity being given by

$$\vec{\sigma}(\vec{k}, -\vec{p}, \omega) = \frac{ie^2}{m\omega} n_0(\vec{k} - \vec{p}) \vec{1} + \frac{e^2}{i\omega} \chi_{j_j}(\vec{k}, -\vec{p}, \omega). \quad (2.10)$$

Just as (2.3) describes the linear response to external potentials, one may define screened correlation functions which give the current response due to the local effective potentials. Using gauge invariance with respect to the effective potentials, we find that $\tilde{\sigma}_{ii}$ in (1.3) is given by

$$\tilde{\sigma}(\vec{k} - \vec{p}, \omega) = \frac{ie^2}{m\omega} n_0(\vec{k} - \vec{p}) \vec{1} + \frac{e^2}{i\omega} \tilde{\chi}_{j_j}(\vec{k}, -\vec{p}, \omega). \quad (2.11)$$

Of course, $\tilde{\chi}_{j_j}$ is not a true response function such as defined in (2.4).

Since the long-range self-consistent field effects are incorporated into the local effective field, in evaluating $\tilde{\sigma}_{ii}$ we need only include the short-ranged screened interactions between electrons.^{5,6} In the so-called RPA one argues that these screened interactions may be neglected. In this approximation, it is reasonable to take $\tilde{\sigma}_{ii}(\vec{k}, -\vec{p}, \omega)$ to be equal to $\sigma_{ii}(\vec{k}, -\vec{p}, \omega)$, the latter being evaluated for a fictitious inhomogeneous system of noninteracting electrons. The RPA should be good at high

frequencies where collisions are unimportant. If a high-frequency expansion of the right-hand side of (2.4) is made, we may prove with great generality that

$$\chi_{jj}(\vec{k}, -\vec{p}, \omega) \sim O(1/\omega^2)$$

by making use of the microscopic definition (2.5). In the RPA, we can immediately conclude from (2.12) that

$$\tilde{\chi}_{jj}(\vec{k}, -\vec{p}, \omega) \sim O(\omega^{-2}), \quad (2.12)$$

and hence arrive at (1.5). In the Appendix, we sketch the equation-of-motion method which gives (1.5) as well as higher-order corrections.

III. STEP-FUNCTION STATIC DENSITY PROFILE: SIMPLE EXAMPLE

Using the results of Secs. I and II, the surface plasmon in the high-frequency limit is seen to correspond to a nontrivial solution of the coupled integral equations ($i = x, y, z$),

$$\delta E_i(\vec{k}, \omega) = \frac{4\pi e^2}{m\omega^2(\omega^2 - c^2k^2)} \sum_j \int \frac{d\vec{p}}{(2\pi)^3} n_0(\vec{k} - \vec{p}) \times (\omega^2 \delta_{ij} - c^2 k_i k_j) \delta E_j(\vec{p}, \omega). \quad (3.1)$$

No assumption has been made concerning the static electronic density $n_0(\vec{R})$, the Fourier transform of which enters into the kernel of (3.1).

In a homogeneous system, we have $n_0(\vec{k}) = n_0 \delta(\vec{k})$ so that (3.1) reduces to a set of well known linear algebraic equations,

$$\delta E_i(\vec{k}, \omega) = \frac{\omega_p^2}{\omega^2 - c^2k^2} \sum_j \left(\delta_{ij} - \frac{c^2 k_i k_j}{\omega^2} \right) \delta E_j(\vec{k}, \omega). \quad (3.2)$$

In this case, it is convenient to decompose the local electric field into longitudinal and transverse parts,

$$\vec{k} \cdot \vec{E}_i(\vec{k}, \omega) = \vec{k} \times \delta \vec{E}_i(\vec{k}, \omega) = 0. \quad (3.3)$$

Then (3.2) may be written

$$\delta \vec{E}_i(\vec{k}, \omega) + \delta \vec{E}_i^{\perp}(\vec{k}, \omega) = \frac{\omega_p^2}{\omega^2 - c^2k^2} \delta \vec{E}_i^{\perp}(\vec{k}, \omega) + \frac{\omega_p^2}{\omega^2} \delta \vec{E}_i^{\parallel}(\vec{k}, \omega). \quad (3.4)$$

The two possible solutions to (3.4) are completely decoupled,

$$\begin{aligned} \delta \vec{E}_i^{\parallel}(\vec{k}, \omega) &\neq 0 \quad \text{if } \omega^2 = \omega_p^2 \\ \delta \vec{E}_i^{\perp}(\vec{k}, \omega) &\neq 0 \quad \text{if } \omega^2 = \omega_p^2 + c^2k^2. \end{aligned} \quad (3.5)$$

In Ref. 4, surface plasmons were discussed using a linear-response correlation-function ap-

proach within the electrostatic approximation. It is easy to obtain our previous results from (3.1) by taking the limit $c \rightarrow \infty$ (i. e., retardation effects are neglected). We are left with

$$\delta E_i(\vec{k}, \omega) = \frac{4\pi e^2}{m\omega^2} \sum_j \frac{k_i k_j}{k^2} \int \frac{d\vec{p}}{(2\pi)^3} n_0(\vec{k} - \vec{p}) \delta E_j(\vec{p}, \omega). \quad (3.6)$$

Making use of the fact that the local electric field is given by

$$e \delta E_i(\vec{k}, \omega) = -ik_i v(k) \delta n(\vec{k}, \omega), \quad (3.7)$$

we see that (3.6) is equivalent to [2.28] of Ref. 4,

$$\delta n(\vec{k}, \omega) = \frac{4\pi e^2}{m\omega^2} \int \frac{d\vec{p}}{(2\pi)^3} n_0(\vec{k} - \vec{p}) \frac{\vec{p} \cdot \vec{k}}{p^2} \delta n(\vec{p}, \omega). \quad (3.8)$$

In the rest of this section, we wish to apply our general result (3.1) to the simple case in which the static electronic density is given by

$$n_0(\vec{R}) = n_0(z) = n_0 \theta(z), \quad (3.9)$$

where $\theta(z)$ is the step function. This calculation is in the way of an illustration. As we have emphasized earlier, the real advantage of our formulation and results such as (3.1) is that one can deal with more realistic density profiles, including the effect of lattice periodicity.

For simplicity, we assume that the surface collective mode is moving along the x direction in the $z = 0$ plane and that $\delta E_y = 0$. Making use of the Fourier transform of (3.9)

$$n_0(\vec{k}) = -i(2\pi)^2 \frac{n_0 \delta(k_x) \delta(k_y)}{k_z - i0^+}, \quad (3.10)$$

we may reduce (3.1) to two coupled one-dimensional singular-integral equations,

$$\begin{aligned} \delta E_x(k_z) &= A_{11}(k_z; q, \omega) \int_{-\infty}^{\infty} \frac{dp_z}{2\pi i} \frac{\delta E_x(p_z)}{p_z - k_z - i0^+} \\ &+ A_{12}(k_z; q, \omega) \int_{-\infty}^{\infty} \frac{dp_z}{2\pi i} \frac{\delta E_z(p_z)}{p_z - k_z - i0^+}, \end{aligned} \quad (3.11)$$

$$\begin{aligned} \delta E_z(k_z) &= A_{22}(k_z; q, \omega) \int_{-\infty}^{\infty} \frac{dp_z}{2\pi i} \frac{\delta E_z(p_z)}{p_z - k_z - i0^+} \\ &+ A_{12}(k_z; q, \omega) \int_{-\infty}^{\infty} \frac{dp_z}{2\pi i} \frac{\delta E_x(p_z)}{p_z - k_z - i0^+}. \end{aligned}$$

We have introduced the following abbreviations:

$$\begin{aligned} A_{11}(k_z; q, \omega) &\equiv -\frac{\omega_p^2(\omega^2 - c^2q^2)}{\omega^2(\omega^2 - c^2q^2 - c^2k_z^2)}, \\ A_{22}(k_z; q, \omega) &\equiv -\frac{\omega_p^2(\omega^2 - c^2k_z^2)}{\omega^2(\omega^2 - c^2q^2 - c^2k_z^2)}, \end{aligned} \quad (3.12)$$

$$A_{12}(k_x; q, \omega) \equiv \frac{\omega_p^2 c^2 k_x q}{\omega^2 (\omega^2 - c^2 q^2 - c^2 k_x^2)} .$$

Since $\omega^2 \leq c^2 q^2$ for the solutions of interest, the A_{ij} coefficients are nonsingular. We also note that

$$\delta E_{x,z}(k_x) \equiv \delta E_{x,z}(q, k_x, \omega)$$

is the Fourier transform of $\delta E_{x,z}(x, z, t)$.

Rather than making use of the general method of solving homogeneous singular-integral equations,⁷ we write down the following ansatz for the solution of (3.11):

$$\delta E_x(z) = E_{\pm}(q) e^{-\kappa_{\pm}|z|}, \quad (3.13)$$

$$\delta E_x(z) = i \operatorname{sgn} z E_{\pm}(q) (\kappa_{\pm}/q) e^{-\kappa_{\pm}|z|}.$$

Here the upper (lower) sign is obtained when $z > 0$ ($z < 0$). For a nontrivial solution of (3.11), κ_+ and κ_- must satisfy a certain relation. This condition will give us the dispersion relation of the surface mode $\omega = \omega(q)$. Our ansatz (3.13) is guided by several criteria. First of all, we recall that within the electrostatic approximation,⁴ we found that the surface plasmon of frequency $\omega_p/\sqrt{2}$ corresponded to electric fields given by (3.13), but with $\kappa_{\pm} = q$. Moreover, we are looking for surface modes in which there is no bulk-charge fluctuation, and thus $\nabla \cdot \delta \vec{E} = 0$ for $z \neq 0$ or

$$q \delta E_x(q, z) = i \frac{\partial}{\partial z} [\delta E_x(q, z)], \quad z \neq 0. \quad (3.14)$$

We emphasize that neither (3.13) nor (3.14) are correct for $z = 0$ since

$$\vec{\nabla} \cdot \delta \vec{E}(x, z) = -4\pi e \delta n(z). \quad (3.15)$$

Taking the Fourier transform of (3.13), we have

$$\delta E_x(k_x) = \frac{(k_x + i\kappa_-)E_+ - (k_x - i\kappa_+)E_-}{i(k_x - i\kappa_+)(k_x + i\kappa_-)}, \quad (3.16)$$

$$\delta E_x(k_x) = \frac{(k_x + i\kappa_-)E_+ \kappa_+ + (k_x - i\kappa_+)E_- \kappa_-}{q(k_x - i\kappa_+)(k_x + i\kappa_-)}.$$

Since $\delta E_{x,z}(z)$ is finite at $z = 0$, we have ignored the contribution from this point in (3.16). Inserting (3.16) into (3.11) and performing the integrals with the aid of Cauchy's residue theorem, we obtain the following linear equations for the field amplitudes E_{\pm} :

$$(k_x + i\kappa_-) \left(\frac{\kappa_+}{q} (1 + A_{11}) + iA_{12} \right) E_+ + (k_x - i\kappa_+) \frac{\kappa_-}{q} E_- = 0, \quad (3.17)$$

$$(k_x + i\kappa_-) \left((1 + A_{22}) - i \frac{\kappa_+}{q} A_{12} \right) E_+ - (k_x - i\kappa_+) E_- = 0.$$

A nontrivial solution is obtained if

$$\left(\frac{\kappa_+}{q} (1 + A_{11}) + \frac{\kappa_-}{q} (1 + A_{22}) \right) + iA_{12} \left(1 - \frac{\kappa_- \kappa_+}{q^2} \right) = 0. \quad (3.18)$$

Since κ_{\pm} and A_{ij} are real, we must have

$$\kappa_+ \kappa_- = q^2 \quad (3.19)$$

as well as

$$\begin{aligned} \kappa_- [\omega^2 (c^2 k_x^2 + c^2 q^2 - \omega^2) + \omega_p^2 (\omega^2 - c^2 k_x^2)] \\ = -\kappa_+ [\omega^2 (c^2 k_x^2 + c^2 q^2 - \omega^2) + \omega_p^2 (\omega^2 - c^2 q^2)]. \end{aligned} \quad (3.20)$$

Since $\kappa_{\pm}(q)$ and $\omega = \omega(q)$ are independent of k_x , we can equate the coefficients of k_x^2 and k_x^0 in (3.20) to 0. This gives us two relations

$$\frac{\kappa_+}{\kappa_-} = (\omega_p^2 - \omega^2)/\omega^2, \quad (3.21)$$

$$\frac{\kappa_+}{\kappa_-} = (c^2 q^2 - \omega^2 + \omega_p^2) \omega^2 / (c^2 q^2 - \omega^2) (\omega_p^2 - \omega^2),$$

from which it directly follows that

$$\omega_p^2 / 2\omega^2 + \omega^2 / 2(\omega^2 - c^2 q^2) = 1. \quad (3.22)$$

Solving this quadratic equation for ω^2 , we find that the solution corresponding to a surface plasmon with retardation effects is the well-known expression

$$\omega^2 = \frac{\omega_p^2}{2} \{ 1 + 2(cq/\omega_p)^2 - [1 + 4(cq/\omega_p)^4]^{1/2} \}. \quad (3.22')$$

The other solution of (3.22) is clearly unphysical. Finally, making use of (3.22) in (3.19), we easily obtain the following relations:

$$c^2 \kappa_-^2 = c^2 q^2 - \omega^2, \quad c^2 \kappa_+^2 = c^2 q^2 + \omega_p^2 - \omega^2. \quad (3.23)$$

This completes our discussion for the simple case of two different media separated by a plane boundary. The results summarized by (3.13), (3.22), and (3.23) may, of course, be easily obtained by matching the tangential components of the electric fields in two homogeneous systems (see, for example, Ref. 1). However, our method can equally well be used to deal with a smooth-transition region, such as described, for example, by the density profile

$$n_0(z) = n_0 (1 - e^{-z/d}) \theta(z). \quad (3.24)$$

The Fourier transform of this is

$$n_0(\vec{k}) = -i(2\pi)^2 \frac{n_0 \delta(k_x) \delta(k_y)}{(k_x - i0^+)(1 + idk_x)}. \quad (3.25)$$

The skin depth "d" is expected to be only a few angstroms. Using (3.25) instead of (3.10) in (3.1), we can easily write down the appropriate coupled

integral equations for $\delta E_{s,z}$. In this case, we will no longer be dealing with Cauchy-type kernels. The solution of such singular-homogeneous integral equations is discussed in Chap. 18 of Ref. 7.

APPENDIX

The main purpose of this appendix is to obtain an equation of motion for the quantum-mechanical Wigner distribution function $f(\vec{p}, \vec{R}, t)$ in an inhomogeneous electron gas. More precisely, this will be done treating the Coulomb and magnetic interactions between electrons in the self-consistent field approximation. We recall that since the average velocity of electrons is much less than the velocity of light, it is quite adequate to use the effective current-current interaction⁶

$$\frac{1}{c^2} \int d\vec{r} \int d\vec{r}' \frac{e^2}{|\vec{r} - \vec{r}'|} \vec{j}(\vec{r}) \cdot \vec{j}(\vec{r}') \quad (\text{A1})$$

to describe the exchange of transverse photons between moving electrons. While the magnetic interaction term (A1) appears to be of order $(v_F/c)^2$ relative to the Coulomb interaction, it actually gives rise to a self-consistent local-field correction which is just as important as that due to the Coulomb interactions. This is discussed in qualitative terms by Pines and Nozières⁵ in the context of homogeneous systems. On the other hand, the *screened* magnetic interaction between electrons is of order $(v_F/c)^2$ relative to the *screened* Coulomb interaction, and thus can be safely neglected. In the RPA, even the *screened* Coulomb interaction is omitted.

It is straightforward to construct the equation of motion for the single-particle Green's function $G_1(1, 2)$ in the presence of external scalar and vector potentials. The electronic self-energy will involve a contribution from the usual Coulomb-interaction term

$$\int d\vec{r} \int d\vec{r}' \frac{e^2}{|\vec{r} - \vec{r}'|} n(\vec{r}) n(\vec{r}') \quad (\text{A2})$$

in addition to (A1). If we use the Hartree decoupling for the two-particle Green's functions, the equation of motion for $G_1(1, 2)$ and its adjoint can be written

$$\left(i \frac{\partial}{\partial t_1} + \frac{\nabla_1^2}{2m} + \frac{ie}{2mc} [\vec{\nabla}_1 \cdot \vec{A}^{\text{ext}}(1) + \vec{A}^{\text{ext}}(1) \cdot \vec{\nabla}_1] + e\phi^{\text{ext}}(1) \right) G_1(1, 2) = \delta(1-2), \quad (\text{A3})$$

$$\left(-i \frac{\partial}{\partial t_2} + \frac{\nabla_2^2}{2m} - \frac{ie}{2mc} [\vec{\nabla}_2 \cdot \vec{A}^{\text{ext}}(2) + \vec{A}^{\text{ext}}(2) \cdot \vec{\nabla}_2] + e\phi^{\text{ext}}(2) \right) G_1(1, 2) = \delta(1-2). \quad (\text{A4})$$

We work to lowest order in the effective vector potential, which is given explicitly in our self-consistent approximation by

$$\vec{A}^{\text{ext}}(1) \equiv \vec{A}^{\text{ext}}(\vec{r}, t) = \vec{A}^{\text{ext}}(\vec{r}, t) + \delta \vec{A}^{\text{loc}}(\vec{r}, t), \quad (\text{A5})$$

with

$$\delta \vec{A}^{\text{loc}}(\vec{r}, t) = -\frac{1}{c} \int d\vec{r}' \frac{1}{|\vec{r} - \vec{r}'|} \delta \vec{j}_P(\vec{r}', t), \quad (\text{A6})$$

Here $\delta \vec{j}_P(\vec{r}, t) \equiv e \delta \vec{j}(\vec{r}, t)$ is the induced paramagnetic current density. The effective scalar potential in the self-consistent field approximation is given by

$$\phi^{\text{eff}}(\vec{r}, t) \equiv \phi_0^{\text{ext}}(\vec{r}) + \delta \phi^{\text{ext}}(\vec{r}, t),$$

where

$$\phi_0^{\text{ext}}(\vec{r}) = \phi_0^{\text{ext}}(\vec{r}) + e^2 \int d\vec{r}' \frac{1}{|\vec{r} - \vec{r}'|} n_0(\vec{r}'), \quad (\text{A7})$$

$$\delta \phi^{\text{ext}}(\vec{r}, t) = \delta \phi_0^{\text{ext}}(\vec{r}, t) + e^2 \int d\vec{r}' \frac{1}{|\vec{r} - \vec{r}'|} \delta n(\vec{r}', t). \quad (\text{A8})$$

The second terms on the right-hand side of (A7) and (A8) will be denoted by $\phi_0^{\text{loc}}(\vec{r})$ and $\delta \phi^{\text{loc}}(\vec{r}, t)$, respectively. We include a time-independent scalar potential $\phi_0^{\text{ext}}(\vec{r})$ since it gives rise to an inhomogeneous static density profile $n_0(\vec{r})$. While we do not linearize with respect to $\phi_0^{\text{ext}}(\vec{r})$, we do assume that $\delta \phi_0^{\text{ext}}(\vec{r}, t)$ and $\vec{A}^{\text{ext}}(\vec{r}, t)$ are small perturbing fields.

Subtracting (A4) from (A3), we may derive an equation for the Wigner distribution function $f(\vec{p}, \vec{R}, T)$ in the same way as discussed in Sec. II of Ref. 4 for the simpler case in which $\vec{A}^{\text{ext}}(\vec{r}, t) = 0$. We obtain

$$\begin{aligned} \delta f(\vec{p}, \vec{k}, \omega) = & e \int \frac{d\vec{p}'}{(2\pi)^3} \frac{[\delta f(\vec{p} - \frac{1}{2}\vec{p}', \vec{k} - \vec{p}', \omega) - \delta f(\vec{p} + \frac{1}{2}\vec{p}', \vec{k} - \vec{p}', \omega)] \phi_0^{\text{ext}}(\vec{p}')}{\omega - \vec{p} \cdot \vec{k} / m} \\ & + e \int \frac{d\vec{p}'}{(2\pi)^3} \frac{[f_0(\vec{p} - \frac{1}{2}\vec{p}', \vec{k} - \vec{p}') - f_0(\vec{p} + \frac{1}{2}\vec{p}', \vec{k} - \vec{p}')] \delta \phi^{\text{ext}}(\vec{p}', \omega)}{\omega - \vec{p} \cdot \vec{k} / m} \end{aligned}$$

$$-\frac{e}{2mc} \int \frac{d\vec{p}'}{(2\pi)^3} \frac{\{f_0(\vec{p}-\frac{1}{2}\vec{p}', \vec{k}-\vec{p}') [2\vec{p}+\vec{k}-\vec{p}'] - f_0(\vec{p}+\frac{1}{2}\vec{p}', \vec{k}-\vec{p}') [2\vec{p}-\vec{k}+\vec{p}']\}}{\omega - \vec{p} \cdot \vec{k}/m} \vec{A}^{\text{eff}}(\vec{p}', \omega), \quad (\text{A9})$$

where

$$\begin{aligned} f(\vec{p}, \vec{k}, \omega) &\equiv \int d\vec{R} \int dT e^{-i\vec{k} \cdot \vec{R} + i\omega T} f(\vec{p}, \vec{R}, T) \\ &= f_0(\vec{p}, \vec{k}) + \delta f(\vec{p}, \vec{k}, \omega). \end{aligned} \quad (\text{A10})$$

The Wigner distribution function $f_0(\vec{p}, \vec{k})$ is determined by Eq. (3.20) of Ref. 4 and will be assumed to be known. In (A9), the local induced potentials are given by (A6) and (A8), namely,

$$\delta \vec{A}^{10c}(\vec{k}, \omega) = -(4\pi e / ck^2) \delta \vec{j}(\vec{k}, \omega), \quad (\text{A11})$$

$$\delta \phi^{10c}(\vec{k}, \omega) = (4\pi e / k^2) \delta n(\vec{k}, \omega), \quad (\text{A12})$$

with

$$\delta n(\vec{k}, \omega) = \int \frac{d\vec{p}}{(2\pi)^3} \delta f(\vec{p}, \vec{k}, \omega), \quad (\text{A13})$$

$$\delta \vec{j}(\vec{k}, \omega) = \int \frac{d\vec{p}}{(2\pi)^3} \left(\frac{\vec{p}}{m} \right) \delta f(\vec{p}, \vec{k}, \omega),$$

In view of (A11)–(A13), we see that (A9) is a closed-integral equation for $\delta f(\vec{p}, \vec{k}, \omega)$. Nontrivial solutions of (A9) in the limit $\delta \phi^{\text{ext}}$ and $\vec{A}^{\text{ext}} \rightarrow 0$ correspond to self-sustaining collective modes.

As in Ref. 4, it is useful to solve (A9) by iteration, treating the second and third terms on the right-hand side as the inhomogeneous terms. This gives $\delta f(\vec{p}, \vec{k}, \omega)$ in terms of a nonlocal linear response to $\delta \phi^{\text{eff}}(\vec{p}', \omega)$ and $\vec{A}^{\text{eff}}(\vec{p}', \omega)$, the kernels being given explicitly by infinite series. Using (A13), the paramagnetic electric current is given by

$$\begin{aligned} \delta \vec{j}_P(\vec{k}, \omega) &= -e^2 \int \frac{d\vec{p}}{(2\pi)^3} \bar{\chi}_{jn}(\vec{k}, -\vec{p}, \omega) \delta \phi^{\text{eff}}(\vec{p}, \omega) \\ &\quad + \frac{e^2}{c} \int \frac{d\vec{p}}{(2\pi)^3} \bar{\chi}_{ji}(\vec{k}, -\vec{p}, \omega) \cdot \vec{A}^{\text{eff}}(\vec{p}, \omega), \end{aligned} \quad (\text{A14})$$

where we have explicit expressions in terms of the static Wigner distribution function $f_0(\vec{p}, \vec{k})$ for $\bar{\chi}_{jn}$ and $\bar{\chi}_{ji}$, as given by the previously mentioned itera-

tion of (A9). Since we are working to lowest order in the perturbing (and induced) potentials, the diamagnetic current in terms of the effective vector potential is simply

$$\delta \vec{j}_D(\vec{r}, t) = -(e^2/mc) n_0(\vec{r}) \vec{A}^{\text{eff}}(\vec{r}, t). \quad (\text{A15})$$

The total electrical current is thus

$$\begin{aligned} \delta \vec{J}(\vec{k}, \omega) &= -\frac{e^2}{mc} \int \frac{d\vec{p}}{(2\pi)^3} n_0(\vec{k}-\vec{p}) \vec{A}^{\text{eff}}(\vec{p}, \omega) \\ &\quad + \delta \vec{j}_P(\vec{k}, \omega). \end{aligned} \quad (\text{A16})$$

One may view the $\bar{\chi}$ functions our procedure gives as the RPA approximation to screened response functions, the latter being *defined* with respect to the true effective potentials by (A14). Making use of gauge invariance relative to the effective potentials, the screened conductivity is given by (2.11) and

$$\delta \vec{E} = -i\vec{p} \delta \phi^{\text{eff}}(\vec{p}, \omega) + (i\omega/c) \vec{A}^{\text{eff}}(\vec{p}, \omega) \quad (\text{A17})$$

is the effective time-dependent electric field which is involved in (1.3) and (1.4).

One may easily obtain the well-known RPA expressions for $\bar{\chi}_{jj}$ and $\bar{\chi}_{jn}$ in a *homogeneous* electron gas using (A9). In this case, $\phi_0^{\text{eff}}(\vec{p}') \propto \delta(\vec{p}')$, and hence the first term on the right-hand side of (A9) vanishes. We are left with

$$\begin{aligned} \delta f(\vec{p}, \vec{k}, \omega) &= e \frac{[f(\vec{p}-\frac{1}{2}\vec{k}) - f(\vec{p}+\frac{1}{2}\vec{k})]}{(\omega - \vec{p} \cdot \vec{k}/m)} \delta \phi^{\text{eff}}(\vec{k}, \omega) \\ &\quad - \frac{e}{2mc} \frac{[f(\vec{p}-\frac{1}{2}\vec{k}) - f(\vec{p}+\frac{1}{2}\vec{k})]}{(\omega - \vec{p} \cdot \vec{k}/m)} \\ &\quad \times 2\vec{p} \cdot \vec{A}^{\text{eff}}(\vec{k}, \omega), \end{aligned} \quad (\text{A18})$$

where $f(p)$ is the Fermi distribution. Multiplying (A18) by $e\vec{p}/m$ and integrating over \vec{p} gives

$$\bar{\chi}_{jn}(\vec{k}, -\vec{p}, \omega) = \delta(\vec{k}-\vec{p}) \int \frac{d\vec{p}'}{(2\pi)^3} \frac{[f(\vec{p}+\frac{1}{2}\vec{k}) - f(\vec{p}'-\frac{1}{2}\vec{k})]}{\omega - \vec{p}' \cdot \vec{k}/m} \left(\frac{\vec{p}'}{m} \right), \quad (\text{A19})$$

$$\bar{\chi}_{ji}(\vec{k}, -\vec{p}, \omega) = \delta(\vec{k}-\vec{p}) \int \frac{d\vec{p}'}{(2\pi)^3} \frac{[f(\vec{p}'+\frac{1}{2}\vec{k}) - f(\vec{p}'-\frac{1}{2}\vec{k})]}{\omega - \vec{p}' \cdot \vec{k}/m} \left(\frac{\vec{p}'}{m} \right) \left(\frac{\vec{p}'}{m} \right).$$

It is easy to verify that these response functions satisfy the key identity⁶ which ensured gauge-invariant results,

$$\begin{aligned} & \left(\tilde{\chi}_{jj}(\vec{k}, -\vec{p}, \omega) - \frac{n_0(\vec{k}-\vec{p})}{m} \right) \vec{p} \\ &= \omega \tilde{\chi}_{jn}(\vec{k}, -\vec{p}, \omega) \quad , \end{aligned} \quad (\text{A20})$$

where we recall that in a homogeneous system $n_0(\vec{k}) = n_0 \delta(\vec{k})$.

Using a procedure analogous to that carried out in Ref. 4, we expand the RPA screened correlation functions in (A14) in powers of $\vec{k} \cdot \vec{p}/\omega$. Making use of

$$\int \frac{d\vec{p}}{(2\pi)^3} \frac{\vec{p}}{m} f_0(\vec{p}, \vec{k}) = 0, \quad \int \frac{d\vec{p}}{(2\pi)^3} f_0(\vec{p}, \vec{k}) = n_0(\vec{k}) \quad , \quad (\text{A21})$$

we find

$$\begin{aligned} \delta_{jP}^{\vec{k}}(\vec{k}, \omega) &= e^2 \int \frac{d\vec{p}}{(2\pi)^3} \left[\frac{1}{\omega} \left(\frac{\vec{p}}{m} \right) n_0(\vec{k}-\vec{p}) + O\left(\frac{1}{\omega^3}\right) \right] \\ &\times \delta\phi^{\text{eff}}(\vec{p}, \omega) + O\left(\frac{1}{\omega^2} \delta\bar{A}^{\text{eff}}\right) \quad . \end{aligned} \quad (\text{A22})$$

We note that these lowest-order results imply

$$\begin{aligned} \tilde{\chi}_{jn}(\vec{k}, -\vec{p}, \omega) &= -(e^2/m) (\vec{p}/\omega) n_0(\vec{k}-\vec{p}) + O(1/\omega^3) \\ \tilde{\chi}_{jj}(\vec{k}, -\vec{p}, \omega) &= O(1/\omega^2) \quad , \end{aligned} \quad (\text{A23})$$

which satisfy (A20) and hence are gauge invariant to order ω^{-1} . While we have not written down the explicit expression for $\tilde{\chi}_{jj}$ to order ω^{-2} , we emphasize that it is quite simple to obtain by using the first iteration of (A9) with

$$\left(\omega - \frac{\vec{p} \cdot \vec{k}}{m} \right)^{-1} = \frac{1}{\omega} + \frac{\vec{p} \cdot \vec{k}}{m\omega^2} + \dots \quad . \quad (\text{A24})$$

Using (A23) in (2.11) we arrive at (1.5), which is the basis of the discussion in Sec. III of this paper.

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Superconducting Transition Temperatures and Lattice Parameters of Simple-Cubic Metastable Te-Au Solutions Containing Fe and Mn[†]

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The superconducting transition temperatures and lattice spacings of simple-cubic Te-Au-Fe and Te-Au-Mn alloys, prepared by rapid quenching from the liquid state, have been measured and correlated with anomalies in the Te-Au system and the band structure proposed to explain those anomalies. The unusual behavior of these properties in the ternary alloys containing Fe and Mn has been interpreted in terms of a Fermi-surface-Brillouin-zone interaction based on information obtained from studying binary Te-Au alloys. The results of this study lend additional support to the electronic band structure proposed for simple-cubic Te-Au alloys, and in addition show a very distinct band-structure effect on the superconducting transition temperatures of the Te-Au-Fe alloys.

I. INTRODUCTION

A recent investigation¹ has shown that the anomalies in the variation of lattice parameter, thermoelectric power, and superconducting transition temperature with concentration in liquid-quenched sim-

ple-cubic Te-Au alloys varying in composition from 60 to 85 at. % Te can be qualitatively explained in terms of a Fermi-surface-Brillouin-zone interaction. Subsequently it was found that about 2 at. % Mn and about 7.5 at. % Fe could be retained in solid solution in quenched Te-Au alloys. The effect of