Dependence of the Normal Modes of Plasma Oscillation at a Bimetallic Interface on the Electron Density Profile*

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Using the high-frequency expansion of the random-phase approximation, we study the normal modes of plasma oscillations at a bimetallic interface. We find that the surface plasmons decay by damping into bulk oscillations of the low-density metal, whose wavelength becomes shorter as the low-density-side density decreases. If the low-density-side electron density is less than approximately a third that on the high-density side, the high-frequency expansion fails because the surface plasmons begin to decay into individual particle-hole states. Thus we are unable to use this expansion to study the modes at metal-vacuum interfaces, where the low-density-side electron density is zero. For bimetallic systems that allow the high-frequency expansion, we show how to determine the dependence of the plasmon dispersion relations on the density profile and stress tensor.

I. INTRODUCTION

By measuring energy loss as a function of angle for electrons transmitted through metallic films[1] or reflected from them[2] it is possible to determine the surface plasmon dispersion relation. Therefore, it is of interest to obtain a theoretical connection between this relation and the structure of the metallic surface.

At long wavelengths, the surface-plasmon dispersion relation takes the form, $\omega^2 = \omega_{sp}^2[1 + Cq + O(q^2)]$, where q is the magnitude of the wave vector parallel to the surface. In a recent publication,[3] the constant ω_{sp}^2 has been shown to be independent of the interfacial electronic density profile, within the random-phase approximation (RPA). The details of the surface structure first appear in the constant C which determines the slope of the dispersion curve at infinite wavelength.

In the past, several authors have derived values of C for unrealistic but simple models of the metal-vacuum interface, in which the electron density drops discontinuously from its value in bulk to zero,[4] or the electron gas is bound in a box with infinitely steep square walls.[5] However, such models avoid the important issue, namely, what we can learn about surface structure from electron scattering experiments.

More recently, Bennett[6] has attempted to go beyond the simplest models by applying hydrodynamic equations to compute C for an electron density which falls off linearly to zero from its bulk value. He obtains a range of values of C corresponding to different values of the surface diffuseness, and finds agreement with both the magnitude and (negative) sign of the best available experimental C (for magnesium) for a not unreasonable diffuseness. The fact that Bennett's value of C can be positive or negative, depending on the diffuseness, is significant; the earlier[4,5] calculated values of C were positive, in disagreement with experiment.

It is doubtful, however, that hydrodynamics describes the low-density region of the surface properly. One of the equations Bennett must use to fix his solution uniquely is, in fact, a boundary condition on the electron velocity at the point where the electron density reaches zero. At, and near, this point, however, hydrodynamic equations cease to describe the system. Thus, although Bennett's results are of the right order of magnitude, a more correct theory remains to be developed.

The fact that all lengths in the surface plasmon problem are of the order of λ_F, the Fermi wavelength, essentially guarantees that C be equal to a constant of order 1 times λ_F. It is therefore not surprising that Bennett's results are of the right order of magnitude, even if hydrodynamics is incorrect.

In attempting to construct a microscopic quantum-mechanical picture of the surface plasmon, we naturally start from the RPA, which has been a most useful tool in describing the collective excitations of the electron gas. The RPA is known, however, to be exact only for a high-density infinite electron gas.[7] One hopes that, despite this fact, it can give an accurate qualitative picture of collective phenomena at suitably chosen interfaces. It seems reasonable, therefore, to embark upon our study of interfacial plasmons by considering a bimetallic rather than a metal-vacuum interface, so that the electron density may be taken to be high throughout the junction.

In order to be able to learn something useful about surface structure from the interfacial plasmon dispersion relation, we wish to express the latter in terms of some simply electronic properties, such as the density profile and stress tensor. This goal cannot be realized unless the high-fre-

quency approximation[8] to the RPA is valid. This approximation, which is based on the assumption that Landau damping of the interfacial plasmon is negligible, enables us to perform the sums on single-particle wave functions which appear in the kernel of the RPA integral equation, and thereby convert it to a much simpler differential equation.

The question of the validity of the high-frequency expansion is discussed below. We find that if the ratio of the low-density-side electron density to that on the high-density side is less than a third, the high-frequency approximation fails—the collective plasma oscillations begin to couple to high-frequency particle-hole states. Thus we arrive at the important if unfortunate conclusion that one must go beyond the high-frequency approximation, if not the RPA, in order to study the metal-vacuum interface.

In a recent preprint, Harris and Griffin[9] claim to have derived a value of C for the surface plasmon at a metal-vacuum interface, using the method of high-frequency expansion of the RPA kernel. They retain only the lowest-order $O(1/\omega^2)$ term in the expansion and obtain a value of C which is given by an undefined integral. The singularity in their integral occurs precisely at the point in space where the local bulk plasma frequency equals the surface plasmon frequency. Such a singularity is a characteristic feature of an interface with a continuous electron density profile. The reason that it occurs only at a single point is that by retaining only $O(1/\omega^2)$ terms in the high-frequency expansion, the bulk plasmon is forced to be dispersionless. Below, we retain terms of up to $O(1/\omega^4)$, and find that the interfacial plasmon is degenerate with a finite-wavelength bulk plasmon at all points for which the local infinite-wavelength bulk plasma frequency is less than the interfacial plasmon frequency. Thus the excitation of a surface plasmon at a bimetallic interface is always accompanied by bulk plasma oscillation in the low-density metal. If the wavelength of this bulk oscillation becomes sufficiently short (which it does if the low-density-side density is less than one-third of the high-side density), the high-frequency expansion fails to converge. Landau damping becomes significant, or in other words, the surface plasmon begins to couple to individual particle-hole states rather than (collective) bulk plasmons in the low-density region. This is the case for the metal-vacuum interface, for which the low-side electron density is zero.

We therefore conclude our study with the presentation of the complete set of equations that describe the bulk and interfacial modes of plasma oscillation in bimetallic systems for which the high-frequency expansion is valid. Our equations are the first to put the surface and bulk modes of a metallic system on the same footing.

In Sec. II of this article we begin our discussion of interfacial plasmons by stating the RPA equation, and by carrying out the high-frequency expansion of its kernel through terms of $O(1/\omega^4)$. In Sec. III, we solve the approximate equation of motion, retaining terms only up to $O(1/\omega^2)$, and find that the solution suggests that surface plasmons are damped by losing energy to bulk plasma excitations. But to this order, the dispersion of the bulk plasmons, which is important in obtaining a correct theory of their coupling to the surface modes, is not taken into account. We proceed, therefore, to study the approximate RPA equation with the $O(1/\omega^4)$ terms retained. In Sec. IV we investigate the qualitative features of the different possible modes of plasma oscillation, bulk and surface. We determine a criterion for the validity of the high-frequency expansion. Then, in Sec. V, we show how to calculate the interfacial plasmon dispersion relation and the bulk plasmon intermetallic transmission coefficient, as functionals of the electron density profile and stress tensor, for systems in which the high-frequency expansion is valid. In Sec. VI we summarize our conclusions.

II. EXPANSION OF RPA KERNEL

The basis of our method is the high-frequency expansion of the RPA, whose validity depends on the fact that collective plasma excitations lie at higher energy than the particle-hole states of which they are linear combinations. This expansion gives the exact RPA infinite-wavelength surface plasmon frequency, as discussed in I (see also Sec. V below).

We quote the RPA equation [Eq. (14) of I] for $\varphi_{q\omega}(z)$, the fluctuating potential associated with an excitation of frequency ω and wave vector $\vec{q}$, as a function of z, the coordinate perpendicular to the surface[10] ($q \equiv |\vec{q}|$) such that

$$\varphi_{q\omega}(z) = \int \frac{d^2k}{(2\pi)^2} \sum_{nn'} \frac{\theta_{kn'} - \theta_{k+qn}}{\omega - \omega_{k+qn} + \omega_{kn'}} \int dz' f_q(z, z') \psi_n(z') \psi_{n'}^*(z') \int dz'' \, \psi_n^*(z'') \psi_{n'}(z'') \varphi_{q\omega}(z'') \, . \tag{1}$$

In Eq. (1), the $\psi_n(z)$ are self-consistent single-particle wave functions satisfying the Hartree equation

$$h\psi_n \equiv \left(-\frac{1}{2m} \frac{d^2}{dz^2} + V_H(z) \right) \psi_n(z) = \omega_n \psi_n(z) \, , \tag{2}$$

where $V_H(z)$ is the Hartree potential. We have defined

$$\omega_{kn} \equiv k^2/2m + \omega_n \ , \qquad \theta_{kn} \equiv \theta(\epsilon_F - \omega_{kn}) \ , \tag{3}$$

where ϵ_F is the Fermi energy. The Coulomb force, Fourier transformed in the coordinate parallel to the surface, is

$$f_q(z, z') \equiv (2\pi e^2/q)\, e^{-q|z-z'|} \ . \tag{4}$$

We now perform the high-frequency expansion of the kernel of Eq. (1). We see that by virtue of the symmetry of the n and n' sums and the $\vec{k}$ integration, the terms odd in $1/\omega$ drop out. To order $1/\omega^4$, we obtain, using the Schrödinger equation, Eq. (2), and the completeness of the ψ_n,

$$\varphi(z) = \frac{1}{\omega^2}\int \frac{d^2k}{(2\pi)^2} \sum_n \theta_{kn'} \int dz' f_q(z, z') \psi^*_{n'}(z') \Big\{ \frac{q^2}{m} + \frac{1}{\omega^2}\left(\frac{3k^2q^4}{2m^3} + \frac{q^6}{4m^3}\right) - \left[2 + \frac{1}{\omega^2}\left(\frac{3k^2q^2}{m^2} + \frac{3q^4}{2m^2}\right)\right] \times [\varphi, h] + \frac{3q^2}{m\omega^2}\,[[\varphi, h], h] - \frac{2}{\omega^2}\,[[[\varphi, h], h], h] \Big\} \psi_{n'}(z') \ . \tag{5}$$

We reduce Eq. (5) to a more comprehensible form by defining the low-order moments of the metallic ground-state density matrix. The electron density profile is

$$n_0(z) = \int \frac{d^2k}{(2\pi)^2} \sum_n \theta_{kn} |\psi_n(z)|^2 \ , \tag{6}$$

while the components of the stress-tensor profile are

$$p_{\parallel}(z) = \int \frac{d^2k}{(2\pi)^2} \sum_n \theta_{kn} \frac{k^2}{2m} |\psi_n(z)|^2 \ , \qquad p_{\perp}(z) = \frac{1}{m}\int \frac{d^2k}{(2\pi)^2} \sum_n \theta_{kn} \left|\frac{d\psi_n}{dz}\right|^2 \ . \tag{7}$$

Let

$$\mathcal{E}(z) = p_{\perp}(z) - \frac{1}{4m}\,\frac{d^2 n_0}{dz^2} \ , \tag{8}$$

then one can easily demonstrate the useful identity

$$n_0 \frac{dV_H}{dz} = -\frac{d\mathcal{E}}{dz} \ , \tag{9}$$

which permits us to eliminate the Hartree potential in favor of the physical quantities, n_0 and $p_{\perp}$.

We evaluate the commutators in Eq. (5), integrate by parts, and use Eqs. (6)–(8), and thus convert Eq. (5) to the form

$$\varphi(z) = \frac{-1}{2q}\int dz'\, e^{-q|z-z'|} \left\{ \frac{d}{dz'}\left[\left(\mathfrak{L} + \frac{4\pi e^2 n_0}{m^2\omega^4}\,\frac{d^2 V_H}{dz'^2}\right)\frac{d}{dz'}\right] - q^2 \mathfrak{L} \right\} \varphi(z') \ , \tag{10}$$

where the (self-adjoint) differential operator $\mathfrak{L}$ is given by

$$\mathfrak{L} = \frac{4\pi e^2}{m\omega^2}\left\{ n_0(z') + \frac{3q^2}{m\omega^2}\, p_{\parallel}(z') + \frac{q^4}{4m^2\omega^2}\, n_0(z') - \frac{d}{dz'}\left[\left(\frac{3}{m\omega^3}\,\mathcal{E} + \frac{q^2}{2m^2\omega^2}\, n_0\right)\frac{d}{dz'}\right] + \frac{1}{4m^2\omega^2}\,\frac{d^2}{dz'^2}\left(n_0 \frac{d^2}{dz'^2}\right)\right\} . \tag{11}$$

Equations (10) and (11) provide the starting point for our analysis of the bimetallic interface.

Note that by retaining terms only up to $O(1/\omega^4)$, i.e., by dropping the last term in

$$\frac{1}{\omega - \Delta\omega} = \frac{1}{\omega} + \frac{\Delta\omega}{\omega^2} + \frac{(\Delta\omega)^2}{\omega^3} + \frac{(\Delta\omega)^3}{\omega^4} + \frac{(\Delta\omega)^4}{\omega^4(\omega - \Delta\omega)} \ , \tag{12}$$

which is the way we derived Eq. (10), we have neglected the effect of Landau damping. If damping is important the last term of Eq. (12) must be retained, at least in an approximate way.

III. DEGENERACY OF SURFACE AND BULK PLASMONS IN $O(1/\omega^2)$ APPROXIMATION

The first evidence that the high-frequency approximation may fail to describe the surface plasmons at a metal-vacuum interface comes from the study

of Eq. (10) with the retention of terms only up to $O(1/\omega^2)$. In this case (cf. I), Eq. (10) becomes

$$\varphi(z) = -\frac{1}{2q}\int dz'\, e^{-q|z-z'|} \times\left[\frac{d}{dz'}\left(\frac{4\pi e^2 n_0(z')}{m\omega^2}\,\frac{d}{dz}\right) - q^2\,\frac{4\pi e^2 n_0(z')}{m\omega^2}\right]\varphi(z')\,, \tag{13}$$

or, integrating by parts,

$$\frac{m\omega^2}{4\pi e^2}\,\varphi(z) = n_0(z)\varphi(z) - \tfrac{1}{2}\int_{-\infty}^{\infty} dz'\, e^{-q|z-z'|}\,\mathrm{sgn}(z-z')\frac{dn_0}{dz'}\,\varphi(z')\,. \tag{14}$$

Suppose that $|qz| \ll 1$, and that $|qa| \ll 1$, where a is a measure of the surface diffuseness. Then we may expand the exponential in Eq. (14) to obtain

$$\left(\frac{m\omega^2}{4\pi e^2} - n_0(z)\right)\varphi(z) = -\tfrac{1}{2}\int_{-\infty}^{\infty} dz'\,\mathrm{sgn}(z-z')\frac{dn_0}{dz'}\,\varphi(z') + \tfrac{1}{2}\,qzA_0 - \tfrac{1}{2}\,qA_1\,, \tag{15}$$

where

$$A_j = \int_{-\infty}^{\infty} dz'\,\frac{dn_0}{dz'}\,(z')^j\,\varphi(z')\,. \tag{16}$$

Differentiating Eq. (15) with respect to z, yields

$$\left(\frac{m\omega^2}{4\pi e^2} - n_0(z)\right)\frac{d\varphi}{dz} = \tfrac{1}{2}\,qA_0\,. \tag{17}$$

By taking advantage of the fact that $n_0(z) \to 0$ rapidly as $z \to \infty$, for a metal-vacuum interface, Eq. (15) may be rewritten as

$$\frac{m\omega^2}{4\pi e^2}\,\varphi(z) = -\tfrac{1}{2}\,A_0 - \int_z^{\infty} dz'\, n_0(z')\frac{d\varphi}{dz'} + \tfrac{1}{2}\,qzA_0 - \tfrac{1}{2}\,qA_1\,. \tag{18}$$

It is now straightforward to obtain a *formal* solution for φ. Substitute Eq. (17) in Eq. (18). This yields

$$\frac{m\omega^2}{4\pi e^2}\,\varphi(z) = -\tfrac{1}{2}\,A_0 + \tfrac{1}{2}\,qzA_0 - \tfrac{1}{2}\,qA_1 - \tfrac{1}{2}\,qA_0\int_z^{\infty} dz'\,\frac{n_0(z')}{m\omega^2/4\pi e^2 - n_0(z')}\,, \tag{19}$$

an equation for $\varphi(z)$, which is not well defined if there exists a $z' \geq z$ for which $n_0(z') = m\omega^2/4\pi e^2$.

Neglecting this problem for the moment, we note that the formal solution for φ and ω is completed by substituting Eq. (19) in Eq. (16), thus obtaining the secular equation for the surface-plasmon frequency,

$$\frac{m\omega^2}{2\pi e^2} = n_\infty - q\int_{-\infty}^{\infty} dz'\,\frac{n_0(z')[n_\infty - n_0(z')]}{m\omega^2/4\pi e^2 - n_0(z')} + q\left(1 - \frac{2\pi e^2 n_\infty}{m\omega^2}\right)\int_{-\infty}^{\infty} dz'\,\frac{dn_0}{dz'}\,z'\,, \tag{20}$$

in which n_∞ is the density deep inside the metal $[n_\infty \equiv n_0(-\infty)]$.

The result of Eq. (20) can be given a meaning by allowing ω^2 to be complex. But rather than press Eq. (20) for a value of ω^2, we prefer to explore the physical significance of the divergent integral on its right-hand side.

The value of z at which the singularity occurs is given by

$$\omega^2 = 4\pi e^2 n_0(z)/m\,, \tag{21}$$

or in other words, the value at which the frequency of the surface oscillation is degenerate with the local bulk plasma frequency. According to Eq. (12), the surface plasma frequency[11] is less than the bulk plasma frequency deep inside the metal by a factor of $1/\sqrt{2} + O(q)$. Therefore there will always exist a point z for an interface with a continuous electron density profile, such that $4\pi e^2 n_0(z)/m$ equals the square of the surface plasmon frequency.

What we have learned from Eq. (20) is that the high-frequency approximation to the RPA predicts that surface plasmons can couple to bulk plasma excitation. We must not, however, be satisfied to solve Eq. (20) for complex ω, and simply to ascribe its imaginary part of damping into bulk plasma excitation. This is because the $O(1/\omega^2)$ approximation misses the important physical effect of dispersion of the bulk plasma excitations.

On the basis of our knowledge of the infinite electron gas we expect a bulk plasmon of (three-dimensional) wave vector $\vec{k}$ to have a frequency $\omega^2 = \omega_p^2(1 + c_0k^2 + c_1k^4 + \cdots)$, where c_0, $c_1, \ldots,$ are positive constants which, in general, may depend on the electron density. The importance of the dispersive terms is that with them, for any z such that the local infinite-wavelength plasma frequency $\omega_p(z)$ is less than the surface plasmon frequency, there exists a bulk plasma excitation of wave vector $\vec{k}$ which is degenerate with the surface plasmon. (This is illustrated in Fig. 1.) In other words, the equation

$$\omega_p^2 = \omega_p^2(z)\,[1 + c_0(z)k^2 + c_1(z)k^4 + \cdots] \tag{22}$$

will have a solution for k^2, for any z such that $\omega_p^2(z)$ is less than or equal to the surface plasmon frequency squared ω_p^2. Thus, a correct estimate of the coupling of surface and bulk plasmons must go beyond the $O(1/\omega^2)$ approximation to the RPA.

IV. QUALITATIVE FEATURES OF THE SOLUTION OF RPA TO $O(1/\omega^4)$ FOR BIMETALLIC INTERFACE

We wish to solve Eq. (10) to $O(q)$ for a bimetallic interface. A schematic representation of the electron density profile of the bimetallic system is given in Fig. 2. The density far to the left n_L is taken to be greater than or equal to the density far to the right n_R.

Integrating by parts, Eq. (10) is transformed into

$$\varphi(z)=\mathfrak{L}\varphi-\frac{1}{2}\int dz'\,\mathrm{sgn}(z-z')\,e^{-q|z-z'|}\times\left[\left(\frac{d\mathfrak{L}}{dz'}\right)\varphi(z')-\frac{4\pi e^2 n_0(z')}{m^2\omega^4}\,\frac{d^2V_H}{dz'^2}\,\frac{d\varphi}{dz'}\right]. \quad (23)$$

Dropping terms of $O(q^2)$, we obtain from Eq. (11) the approximate expression

$$\mathfrak{L}=\frac{4\pi e^2}{m\omega^2}\left[n_0(z)-\frac{3}{m\omega^2}\,\frac{d}{dz}\left(\mathcal{S}(z)\frac{d}{dz}\right)+\frac{1}{4m^2\omega^2}\,\frac{d^2}{dz^2}\left(n_0\frac{d^2}{dz^2}\right)\right]. \quad (24)$$

We begin by examining the solutions φ in the asymptotic regions $z\to\pm\infty$. The analysis is simplified if we assume that n_0, $\mathcal{S}$, and V_H are constant for z outside the region $-\frac{1}{2}a<z<\frac{1}{2}a$, where a is a measure of the surface diffuseness. With this assumption we have, for $z<-\frac{1}{2}a$,

$$\varphi(z)=\frac{\omega_p^{L2}}{\omega^2}\left(1-\frac{\beta_L^2}{\omega^2}\,\frac{d^2}{dz^2}+\frac{1}{4m^2\omega^2}\,\frac{d^4}{dz^4}\right)\varphi+\tfrac{1}{2}\,e^{qz}\int_{-a/2}^{a/2}dz'\,e^{qz'}\left[\left(\frac{d\mathfrak{L}}{dz'}\right)\varphi(z')-\frac{4\pi e^2 n_0(z')}{m^4\omega^4}\,\frac{d^2V_H}{dz'^2}\,\frac{d\varphi}{dz'}\right]. \quad (25)$$

The constant $\beta_L^2\equiv 3\mathcal{S}(-\infty)/mn_0(-\infty)$. Using the definitions (8) and (7), it is straightforward to show[12] that $\beta_L^2=\frac{3}{5}v_F^{L2}$, where v_F^L is the Fermi velocity for the metal on the left. The bulk plasma frequency on the left is $\omega_P^L=(4\pi e^2 n_L/m)^{1/2}$.

The most general solution to Eq. (25) is

$$\varphi(z)=\sum_{j=1}^{4}c_j^L e^{i\gamma_j^L z}+C_L e^{qz}, \quad (26)$$

where the γ_j^L are the four solutions of

$$\omega^2=\omega_p^{L2}\left(1+\frac{\beta_L^2\gamma^2}{\omega^2}+\frac{1}{4m^2\omega^2}\,\gamma^4\right), \quad (27)$$

$$C_L=\frac{1}{2[1-\omega_p^{L2}/\omega^2+O(q^2)]}\int_{-a/2}^{a/2}dz'\,e^{qz'}\times\left[\left(\frac{d\mathfrak{L}}{dz'}\right)\varphi(z')-\frac{4\pi e^2 n_0(z')}{m^2\omega^4}\,\frac{d^2V_H}{dz'^2}\,\frac{d\varphi}{dz'}\right], \quad (28)$$

and the constants c_j^L are to be determined by satisfying boundary conditions.

In order to see what kinds of oscillation may exist for $z<-\frac{1}{2}a$, we study the γ_j^L. The solutions to Eq. (27) are

$$\gamma=\pm\left(2m^2\left\{-\beta_L^2\pm\left[\beta_L^4+\frac{\omega^2}{m^2}\left(\frac{\omega^2}{\omega_p^{L2}}-1\right)\right]^{1/2}\right\}\right)^{1/2}. \quad (29)$$

Two cases occur:

(a) If $\omega^2>\omega_p^{L2}$, then two of the γ_j^L are real and two are imaginary. The boundary condition that φ not diverge at $z=-\infty$ forces only one of the c_j^L to vanish. The fact that two of the γ_j^L are real means that for $\omega^2>\omega_p^{L2}$ there is a bulk plasma wave in the high-density metal.

(b) If $\omega^2<\omega_p^{L2}$, then two of the γ_j^L have imaginary parts greater than zero and two have imaginary parts less than zero. The boundary condition that φ not diverge as $z\to-\infty$ forces two of the c_j^L to vanish. The fact that φ now dies off exponentially as $z\to-\infty$ means that for $\omega^2<\omega_p^{L2}$ the plasma excitation is localized near the interface on the high-density side.

The situation for $z>\frac{1}{2}a$ is precisely analogous to that for $z<-\frac{1}{2}a$. In the above discussion, simply substitute ω_p^R for ω_p^L, β_R for β_L, c_j^R for c_j^L, and note that

$$C_R=\frac{-1}{2[1-\omega_p^{L2}/\omega^2+O(q^2)]}\int_{-a/2}^{a/2}dz'\,e^{-qz'}\times\left(\frac{d\mathfrak{L}}{dz'}\,\varphi(z')-\frac{4\pi e^2 n_0(z')}{m^2\omega^4}\,\frac{d^2V_H}{dz'^2}\,\frac{d\varphi}{dz'}\right). \quad (30)$$

Therefore there are three possibilities [referred to, henceforth, as possibilities (i), (ii), and (iii), respectively, and depicted in Fig. 3].

(i) If $\omega^2>\omega_p^{L2}$, then, by the assumption that $\omega_p^{L2}>\omega_p^{R2}$ the fluctuating potential φ varies sinusoidally for either $z\to\pm\infty$. A mode with $\omega^2>\omega_p^{L2}$ is therefore a bulk plasma mode incident from the left or right, depending on the choice of boundary conditions, with reflection and transmission at the surface.

(ii) If $\omega_p^{L2}>\omega^2>\omega_p^{R2}$, then φ varies sinusoidally as $z\to\infty$ and dies off exponentially as $z\to-\infty$. This mode is therefore either a surface plasmon losing energy by decaying into a bulk plasmon of the low-density metal, or a bulk plasmon incident from the right and reflected at the interface, again depending on the choice of boundary conditions at $z=+\infty$.

(iii) If $\omega^2<\omega_p^{R2}$, then φ is localized at the interface. We shall show in Sec. V, that the frequency

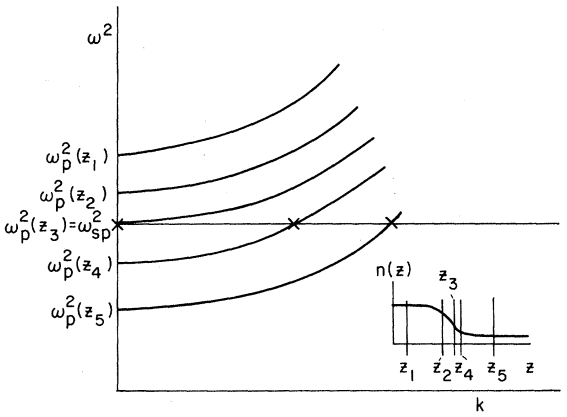

FIG. 1. Schematic drawing for a bimetallic junction of the bulk plasmon dispersion relation appropriate to the five local densities shown in the insert. For sufficiently large z, the bulk plasmon of some wave number k is degenerate with the surface plasmon frequency ω_{sp}. As the local infinite-wavelength bulk plasma frequency decreases, this wave vector increases. Thus, the smaller n_R is, the shorter the wavelength will be of the bulk plasmon deep in the low-density metal which is degenerate with the surface plasmon.

of a surface plasmon is given by $\omega^2=\frac{1}{2}(\omega_p^{L2}+\omega_p^{R2})+O(q)$, which by assumption is greater than ω_p^{R2}. Therefore the case $\omega^2<\omega_p^{R2}$ cannot be realized.

We turn now to a discussion of the solution for φ, in the region $-\frac{1}{2}a<z<\frac{1}{2}a$. Once we know this solution, by matching at $z=\pm\frac{1}{2}a$, we will be able to determine the dispersion relation for the surface mode of oscillation [possibility (ii)], and the transmission and reflection coefficients for the bulk plasmons [possibility (i)].

In the interfacial region, Eq. (23) may be solved in powers of q, by expanding $e^{-q|z-z'|}$. This is valid since $qa\ll 1$. To $O(q)$ and integrating by parts, the expansion yields

$$\varphi=-\tfrac{1}{2}A_0+\tfrac{1}{2}qzA_0-\tfrac{1}{2}qA_1+\mathfrak{L}\varphi\Big|_{z=a/2}$$

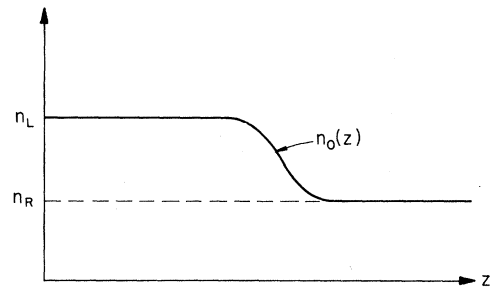

FIG. 2. Schematic drawing of the electron density profile at a bimetallic interface.

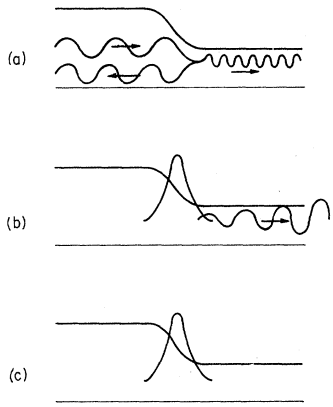

FIG. 3. Possible plasmon modes at a bimetallic interface. (a) Bulk plasmon [referred to as possibility (i) in the text]. (b) Surface plasmon decaying by loss of energy into a bulk plasmon of the low-density metal [referred to as possibility (ii) in the text]. (c) Charge oscillation localized at the surface [referred to as possibility (iii) in the text]. This possibility is never realized.

$$-\int_z^{a/2}dz'\left(\mathfrak{L}+\frac{4\pi e^2n_0\,dz'}{m^2\omega^4}\,\frac{d^2V_H}{dz'^2}\right)\frac{d\varphi}{dz'}\,, \qquad (31)$$

where now

$$A_j\equiv\int_{-a/2}^{a/2}dz'(z')^j\left[\left(\frac{d\mathfrak{L}}{dz'}\right)\varphi(z')-\frac{4\pi e^2n_0(z')}{m^2\omega^4}\,\frac{d^2V_H}{dz'^2}\,\frac{d\varphi}{dz'}\right]. \qquad (32)$$

Our method of solution is as follows: Differentiate Eq. (31) with respect to z. This yields the equation for $u\equiv d\varphi/dz$,

$$u=\tfrac{1}{2}qA_0+\left(\mathfrak{L}+\frac{4\pi e^2n_0(z)}{m^2\omega^4}\,\frac{d^2V_H}{dz^2}\right)u\,, \qquad (33)$$

an inhomogeneous linear fourth-order differential equation. Its solution depends on four arbitrary constants K_j. Substitute the solution to Eq. (33) into Eq. (31) to obtain φ. The constants K_j are now fixed by matching, at $z=\pm\frac{1}{2}a$, to the right- and left-hand solutions found earlier.

Two linear equations for A_0 and A_1 in terms of themselves are obtained by substituting the resulting φ into Eq. (32). These two equations together with four matching conditions (since $\mathfrak{L}$ is a fourth-order differential operator) at each of $z=\pm\frac{1}{2}a$ determine the dispersion relation in the case of the surface mode and the transmission coefficient in that of the bulk mode. The details of this procedure are described in Sec. V.

Finally, let us examine the validity of the high-frequency expansion. The crucial question is whether or not the wavelength of a collective oscil-

lation is sufficiently short to cause it to be Landau damped. A study of the modes of an infinite electron gas suggests[13] that modes whose wavelengths are of the order of or smaller than the Fermi wavelength are Landau damped. A glance at Fig. 1, moreover, reveals that the wavelength of the bulk excitation to which a surface plasmon is coupled [cf. possibility (ii)] becomes shorter if the low-density-side electron density decreases. This is equally clear if we examine the equation [cf. Eq. (27)] for the wave number of the bulk mode induced in the right-hand metal:

$$\omega_{sp}^2 = \omega_p^{R2}\left(1+\frac{\beta_R^2}{\omega_{sp}^2}\gamma^2+\frac{1}{4m^2\omega_{sp}^2}\gamma^4\right), \tag{34}$$

where ω_{sp} is the surface plasmon frequency. In Sec. V we will see[14] that

$$\omega_{sp}^2 \approx \tfrac{1}{2}(\omega_p^{R2}+\omega_p^{L2}). \tag{35}$$

Thus, as the low-density-side electron density n_R decreases to zero, ω_p^{R2} and β_R^2 decrease to zero, while ω_{sp}^2 approaches a constant. This implies, according to Eq. (34), that γ^2 becomes very large as $n_R \to 0$.

Landau damping will be important if $\gamma^2/2m \geq \omega_{sp}$.[15] Neglecting the term in β_R^2 in Eq. (34) (which is small when $n_R \to 0$), this criterion reduces to

$$\omega_{sp}^2/\omega_p^{R2} - 1 \geq 1$$

which implies, using Eq. (35), that

$$\omega_p^{R2} \leq \tfrac{1}{3}\omega_p^{L2}. \tag{36}$$

Thus, if $n_R \lesssim \frac{1}{3}n_L$, the bulk plasmon induced by the surface mode will have such a short wavelength that it cannot be described by the high-frequency approximation.

Therefore, for interfaces such that $n_R \lesssim \frac{1}{3}n_L$, we have concluded that the surface mode is damped into particle-hole excitations in the low-density region. However, the matrix elements for the coupling of surface and individual particle-hole states are not known in terms of any simple properties of the surface structure. Consequently, we are not able, at present, to give a useful formula for the surface plasmon dispersion relation for system with $n_R \lesssim \frac{1}{3}n_L$. This class of systems includes, unfortunately, the important case of the metal-vacuum interface, for which $n_R = 0$. Although in this case, there is no right-hand metal, the conclusions we drew above by studying Eq. (34) remain valid if we interpret this equation within a local density, or WKB picture. Since our conclusion from Eq. (34) was that γ becomes large as the density drops off, the WKB picture must be true sufficiently far out in the low-density tail for the metal-vacuum interface.

V. CALCULATION OF INTERFACIAL PLASMON DISPERSION AND BULK PLASMON TRANSMISSION AT A BIMETALLIC INTERFACE

In this section we elaborate on the remarks of Sec. IV to show how Eq. (23) is solved for a model bimetallic interface, and thus, how the dependence of the normal modes on the surface structure is derived.

To begin, we study the interfacial plasmon, for which $\omega_p^{L2} > \omega^2 > \omega_p^{R2}$. In this case, according to the discussion following Eq. (29), two of the c_j^L are forced to be zero by the condition, $|\varphi(-\infty)| < \infty$, and one of the c_j^R is forced to be zero by $|\varphi(+\infty)| < \infty$. Thus, there are five constants c_j^R and c_j^L still to be determined. The interfacial region's solution for φ contains four undetermined constants, the K_j. The total number of matching conditions at $z = \pm\frac{1}{2}a$ is eight. Thus we have nine constants to determine, and only eight equations. An additional condition on the constants is necessary to fix the dispersion relation for the interfacial plasmon.

The reason that there are three nonvanishing c_j^R, we remember, is that $\omega^2 > \omega_p^{R2}$ implies that φ is sinusoidally varying at $z \to +\infty$. By imposing the condition of outgoing waves, or incoming waves, or reflection at $z = \infty$, we can fix one of the c_j^R, and reduce the number of undetermined constants. In this case we obtain a secular equation which gives the surface plasmon dispersion relations corresponding to a decaying surface mode, a growing mode with energy input from $z = \infty$, or a standing-surface mode. If we impose no condition at ∞, the physical situation corresponds to a bulk plasmon incident from the right with reflection and energy loss to a surface mode. In this case we do not obtain a secular equation for ω^2. Rather ω^2 is given in terms of the bulk plasmon wave number γ by

$$\omega^2 = \omega_p^{R2}\left(1+\frac{\beta_R^2}{\omega^2}\gamma^2+\frac{1}{4m^2\omega^2}\gamma^4\right),$$

and the solution of the matching equation yields the coefficient of reflection of the plasmon from the surface.

Let us assume, for example, that we have imposed a reflection condition at $z \to \infty$ such that $\varphi(z \to \infty) \to \sin(\gamma_z + \delta)$. There are then eight undetermined constants in φ and eight matching conditions, which implies that we are able to obtain the dispersion relation for the interfacial plasmon. We now show how this relation depends functionally on $u(z) \equiv d\varphi/dz$, following the method described in Sec. IV.

Matching conditions on u follow directly from the conditions on φ and imply that the inhomogeneous equation (33) for u has a unique solution, which is proportional to the constant $\frac{1}{2}qA_0$. Substitute Eq. (33) in Eq. (31), to yield

$$\varphi = -\tfrac{1}{2}(A_0 + qA_1) + \mathcal{L}\varphi\big|_{a/2} + \tfrac{1}{4}qa\,A_0 - \int_z^{a/2} dz'\,u(z') \quad . \tag{37}$$

The fact that u is of $O(q)$ means that only the terms $-\frac{1}{2}A_0$ and $\mathcal{L}\varphi|_{a/2}$ on the right-hand side of Eq. (37) are of $O(1)$.

We now use Eq. (37) in Eq. (32) to obtain equations for A_0 and A_1 in terms of themselves. Since we are keeping only up to $O(q)$, we need A_1 only to $O(1)$. Thus

$$A_1 = \int_{-a/2}^{a/2} dz'\,z' \left[\left(\frac{d\mathcal{L}}{dz'}\right)\left(-\tfrac{1}{2}A_0 + \mathcal{L}\varphi\big|_{a/2}\right)\right] . \tag{38}$$

The expression for $d\mathcal{L}/dz$ is [cf. Eq. (24)]

$$\frac{d\mathcal{L}}{dz'} = \frac{4\pi e^2}{m\omega^2}\left[\frac{dn_0}{dz'} - \frac{3}{m\omega^2}\frac{d}{dz'}\left(\frac{d\mathcal{E}}{dz'}\frac{d}{dz'}\right) + \frac{1}{4m^2\omega^2}\frac{d^2}{dz'^2}\left(\frac{dn_0}{dz'}\frac{d^2}{dz'^2}\right)\right] . \tag{39}$$

Therefore,

$$A_1 = \left(-\tfrac{1}{2}A_0 + \mathcal{L}\varphi\big|_{a/2}\right)\int_{-a/2}^{a/2} dz'\,z'\,\frac{dn_0}{dz'} \quad . \tag{40}$$

To obtain a simple equation for A_0, we integrate by parts in Eq. (32), yielding

$$A_0 = \mathcal{L}\varphi\,\big|_{-a/2}^{a/2} - \int_{-a/2}^{a/2} dz'\,(u - \tfrac{1}{2}qA_0) . \tag{41}$$

Using the definition of $\mathcal{L}$, Eq. (24), and using Eq. (37), we have

$$\mathcal{L}\varphi = \frac{4\pi e^2 n_0(z)}{m\omega^2}\left[-\tfrac{1}{2}(A_0 + qA_1) + \mathcal{L}\varphi\,\big|_{a/2} + \tfrac{1}{4}qaA_0 - \int_z^{a/2} dz'\,u(z')\right] + v(z) \quad , \tag{42}$$

where we have defined

$$v(z) \equiv \frac{4\pi e^2}{m\omega^2}\left[-\frac{3}{m\omega^2}\frac{d}{dz}(\mathcal{E}u) + \frac{1}{4m\omega^2}\frac{d^2}{dz^2}\left(n_0\frac{du}{dz}\right)\right] . \tag{43}$$

According to Eq. (42),

$$\mathcal{L}\varphi\big|_{a/2} = \frac{\omega_p^{R2}}{\omega^2}\left[-\tfrac{1}{2}(A_0 + qA_1) + \mathcal{L}\varphi\big|_{a/2} + \tfrac{1}{4}qaA_0\right] + v(\tfrac{1}{2}a) \quad , \tag{44}$$

$$\mathcal{L}\varphi\big|_{-a/2} = \frac{\omega_p^{L2}}{\omega^2}\left[-\tfrac{1}{2}(A_0 + qA_1) + \mathcal{L}\varphi\big|_{a/2} + \tfrac{1}{4}qaA_0 - \int_{-a/2}^{a/2} dz\,u(z)\right] + v(-\tfrac{1}{2}a) \quad .$$

We substitute Eqs. (44) in Eq. (41) and obtain

$$1 = \frac{1}{2}\left(\frac{\omega_p^{L2} - \omega_p^{R2}}{\omega^2 - \omega_p^{R2}}\right)\left(1 - \frac{q}{2}\frac{\omega^2}{\omega^2 - \omega_p^{R2}}\int_{-a/2}^{a/2} dz\,z\,\frac{dn_0}{dz}\right) + \frac{qa}{4}\left(\frac{\omega^2 - \omega_p^{L2}}{\omega^2 - \omega_p^{R2}}\right)\frac{\omega_p^{R2}}{\omega^2} + \left(\frac{\omega^2 - \omega_p^{L2}}{\omega^2 - \omega_p^{R2}}\right)v\left(\frac{a}{2}\right) - v\left(-\frac{a}{2}\right) - \left(1 - \frac{\omega_p^{L2}}{\omega^2}\right)\left(\int_{-a/2}^{-a/2} dz\,\frac{u(z)}{A_0} - \frac{1}{4}qa\right) \quad . \tag{45}$$

Solve Eq. (45) for $\omega = \omega(q)$ to $O(q)$. This yields the dispersion relation

$$\omega^2 = \tfrac{1}{2}(\omega_p^{R2} + \omega_p^{L2})\left[1 + \tfrac{1}{2}q\int_{-a/2}^{a/2} dz\,z\,\frac{dn_0}{dz} - \left(\frac{\omega_p^{L2} - \omega_p^{R2}}{\omega_p^{L2} + \omega_p^{R2}}\right)\left[\tfrac{1}{4}qa + v(\tfrac{1}{2}a) + v(-\tfrac{1}{2}a)\right] + \left(\frac{\omega_p^{L2} - \omega_p^{R2}}{\omega_p^{L2} + \omega_p^{R2}}\right)^2\int_{-a/2}^{a/2} dz\,\frac{u(z)}{A_0}\right] \quad . \tag{46}$$

The $O(1)$ term of Eq. (46) is just the "classical" surface plasmon frequency for the bimetallic interface.[16] The remaining terms give corrections of $O(q)$.

Thus, we determine the dependence of the slope of the interfacial plasmon frequency in terms of $n_0(z)$ and $\mathcal{E}(z)$. The fluctuating field u is obtained by solving Eq. (33) and applying matching and boundary conditions. The slope is then given by the coefficient of q in Eq. (46).

We must remember, however, that Eq. (46) only has meaning if n_R/n_L is greater than about $\frac{1}{3}$. Otherwise, the high-frequency expansion used to derive (46) is invalid.

Finally, we discuss possibility (i), $\omega^2 > \omega_p^{L2}$, which corresponds to bulk plasma oscillation with transmission and reflection at the interface. If $\omega^2 > \omega_p^{L2} > \omega_p^{R2}$, then only one c_j^L and one c_j^R must vanish because of the requirement the φ not diverge at $z = \pm\infty$. If we now impose a physical constraint, say that of outgoing waves at $z \to +\infty$, we reduce the total number of undetermined constants in φ to nine. Thus the satisfaction of the eight matching conditions does not yield a secular equation. For any wave number γ_L there is a bulk plasma mode satisfying

$$\omega^2 = \omega_p^{L2}\left(1 + \frac{\beta_L^2}{\omega^2}\gamma_L^2 + \frac{1}{4m^2\omega^2}\gamma_L^4\right) \quad .$$

The matching conditions fix the coefficient of transmission of the bulk mode for the surface.

That is, we now solve for φ, with the condition that the c_g^L multiplying $e^{i|\gamma_L|z}$ equal 1. This implies a unit incident amplitude of bulk plasmon from the

left. Equation (33) is solved for u and the eight matching equations are solved for the eight remaining constants. The self-consistent equations for A_0 and A_1 are solved as above, but now remembering that u is not of $O(q)$, but contains a component of $O(1)$. The coefficient c_j^R corresponding to the outgoing wave $e^{i|\gamma_R|z}$ is obtained by this procedure. It is the transmission coefficient. We obtain at the same time, of course, the reflection coefficient, the c_j^L which multiplies $e^{-i|\gamma_L|z}$.

VI. CONCLUSION

As long as the high-frequency expansion to the RPA is valid, we may obtain expressions for the dispersion of surface plasmons and the transmission and reflection coefficients of bulk plasmons in a bimetallic system, which depend only on average properties of the electron wave function. As the ratio of the electron densities in the two metals differs too much from 1, the modes of the system begin to couple to individual particle-hole excitations, whose density of states do not seem to be related in any simple way to these average features. Because of this "Landau damping" effect, then, it is difficult to extend our analysis of the plasma oscillations at a bimetallic interface to those of a metal-vacuum interface.

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[11]If $n_0(z) = n_\infty = \text{const}$ for $z < 0$, then the bulk plasmon $\varphi(z)$ is derived from Eq. (15) by imposing the condition

$$\int_0^\infty dz \, \frac{dn_0}{dz} \, \varphi(z) = 0.$$

[12]In bulk,

$$p_\perp \equiv \int_{k<k_F} \frac{d^3k}{(2\pi)^3} \frac{k_z^2}{m} = \frac{1}{3m} \frac{4\pi}{8\pi^3} \tfrac{1}{5} k_F^5 = \tfrac{1}{5} m v_F^2 n_\infty \ ,$$

with $n_\infty \equiv k_F^3/6\pi^2$.

[13]In an infinite system, the RPA energy denominator, $\omega - \omega_{k+qn} + \omega_{kn}$, becomes $\omega - v_F k \cos\theta - k^2/2m$, where k is the three-dimensional wave vector and $-\pi < \theta < \pi$. The high-frequency expansion is valid only if $\omega \gg |v_F k| + k^2/2m$. Thus, it is not valid if $k^2 \approx 2m\omega$. For such short wavelengths, Landau damping is important.

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Exchange Corrections to Hot-Electron Lifetimes*

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We obtain an improved approximation for the inverse vertex function $\epsilon_{\vec{k}t}(\vec{\kappa}, \omega)$ with exchange corrections. The imaginary part of the self-energy of hot electrons is calculated and compared with the random-phase-approximation (RPA) values. The RPA results differ significantly from Quinn's earlier RPA results owing to improved computational facilities. The mean free path of an electron 5 eV above the Fermi surface in aluminum is compared with Kanter's experimental value.

I. INTRODUCTION

Although exchange-corrected dielectric functions[1] $\epsilon_{tt}(\kappa, \omega)$ have been used to calculate the pair distribution function[2-4] and correlation energy of an electron gas[2,5,6] and phonon dispersion curves of metals,[7-9] the effect of using exchange-corrected vertex functions $\Lambda_{\vec{k}}(\vec{\kappa}, \omega) = 1/\epsilon_{\vec{k}t}(\vec{\kappa}, \omega)$ on the electron self-energy has not heretofore been calculated. The present calculation of the imaginary part of the self-energy has been stimulated by Kanter's[10] recent measurement of the mean free path (MFP) of electrons 5 eV above the Fermi surface in aluminum. The MFP is inversely proportional to the