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Surface-plasmon dispersion relation from the reflectivity of parallel-polarized light

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We show that a very general method of deriving the surface-plasmon dispersion relation, $\omega = \omega(Q)$, for a semi-infinite metal is to set either $r_p(q_z) = \infty$ or $r_p(-q_z) = 0$, where r_p is the reflected amplitude of parallel-polarized light and $q_z = i(Q^2 - \omega^2/c^2)^{1/2}$. This method is applied to get a new formula for the dispersion in the retardation region for a surface with a continuously varying electron-density profile, and it reduces to the Harris-Griffin result in the $c \to \infty$ limit.

I. INTRODUCTION

It was pointed out by Cardona[1] that if one lets $r_p \to \infty$, where r_p is the Fresnel expression[2] for the reflection amplitude of parallel-polarized light, i.e., light having its electric field in the plane of incidence, one arrives at the well-known[3-5] dispersion relation of surface plasmons (SP) for a plane interface between a semi-infinite metal and vacuum, viz.,

$$Q^2 = (\omega^2/c^2)\epsilon(\omega)/[\epsilon(\omega)+1] , \tag{1}$$

where ω and Q are, respectively, the frequency and wave vector (parallel to the surface) of the SP and $\epsilon(\omega)$ is the dielectric constant of the metal. The procedure can be understood physically as corresponding to a resonance: an electromagnetic wave can be excited near the surface without any incident wave, and this wave is precisely the surface plasmon. In the nonretardation approximation ($Q \gg \omega/c$), Eq. (1) leads to the familiar relationship $\epsilon(\omega) = -1$. Sauter,[6] on the other hand, derived a more general SP dispersion relation than Eq. (1), including some nonlocal corrections, by equating to *zero* his expression for r_p which included the possibility of photoexcitation of bulk plasmons. Thus, while there seems to be an intimate connection between r_p and the SP dispersion relation, the issue remains somewhat confusing. In this note we try to clarify the point by showing that the SP dispersion relation can be obtained either by setting $r_p(q_z)$ to infinity, or by setting $r_p(-q_z)$ to zero, where $q_z = (\omega^2/c^2 - Q^2)^{1/2}$ is the z component of the wave vector on the vacuum side of the interface. This result is the consequence of a simple, reciprocal relationship which exists between $r_p(-q_z)$ and $r_p(q_z)$, as we shall prove below. For a surface wave, q_z is purely imaginary so that $r_p(-q_z) = r_p(q_z^*)$. By using either of the criteria mentioned above, one arrives at different versions of the SP dispersion relation depending solely on the choice of r_p. Thus, for example, if we use the expression for $r_p(q_z)$ derived by Kliewer and Fuchs (KF),[7] we obtain their form of the SP dispersion relation. In Sec. II, we apply the condition $r_p(-q_z) = 0$ to the expression for r_p derived by recent, microscopic theories,[8,9] and thereby obtain a new and general SP dispersion relation which reduces to the result given by Harris and Griffin[10] for an arbitrary density profile in the limit of no retardation.

To establish the reciprocal relationship connecting $r_p(q_z)$ and $r_p(-q_z)$, we note that regardless of the model chosen to represent the electronic density distribution near the metal-vacuum interface, the electric field components must satisfy the following equation on the vacuum side very far from the surface (i.e., for $z \to -\infty$ where the metal occupies the half space $z > 0$):

$$\frac{d^2E}{dz^2} + q_z^2 E = 0 . \tag{2}$$

For p-polarized light incident on the metal in the x-z plane, the asymptotic form of the solution can be written

$$E_x(z, q_z) \sim e^{iq_z z} - r_p(q_z) e^{-iq_z z} . \tag{3}$$

The reflection amplitude r_p depends, in fact, on the frequency of radiation, the angle of incidence and the dielectric properties of the metal. For a given metal, it can be regarded as a function of ω and q_z. If we let $q_z \to -q_z$, $E_x(z, -q_z)$ must be a solution of Eq. (2) also, and its Wronskian with $E_x(z, q_z)$ must be independent of z over the entire region of validity of Eq. (2). Calling the Wronskian $C(q_z)$, one easily finds that

$$r_p(-q_z) = \frac{1}{r_p(q_z)}\left(1 - \frac{iC(q_z)}{q_z}\right) . \tag{4}$$

Furthermore, if the model has a sharp boundary separating the vacuum region from the metal, one can go one step further and show that $C(q_z)$ is identically zero. Equation (4) implies that the conditions $r_p(q_z)\to\infty$ and $r_p(-q_z)=0$ are indeed equivalent, thus clarifying Sauter's procedure[6] and bringing it in agreement with Cardona's argument.[1] For a surface wave, q_z is purely imaginary, and the reciprocal relationship of Eq. (4) is reminiscent of the properties of angular-momentum-resolved S-matrix elements in quantum scattering theory.[11]

From a physical point of view, it is clear why both $r_p(q_z)\to\infty$ and $r_p(-q_z)=0$ are conditions for the presence of a surface mode. The first condition means that there is a reflected wave in the absence of an incident wave, and the positive sign of q_z must be chosen so that when it is analytically continued to the imaginary axis, the field may decay exponentially away from the surface. The second condition, on the other hand, means that only the incident wave is present on the vacuum side, and q_z must now be analytically continued to the negative imaginary axis in order to produce a decaying field. We should emphasize that the condition for a surface mode corresponds to a complex angle of incidence, and we cannot excite surface plasmons simply by reflecting p-polarized light. A complex angle of incidence, however, can be experimentally achieved in attenuated total-reflection (ATR) measurements.[12-14] The evanescent wave in that case does not excite the surface plasmon; it *is*, from our point of view, the SP wave on the vacuum side.

II. APPLICATION

As a simple application of our procedure, consider the expression for r_p given by Kliewer and Fuchs[7] for the model of a metal with a sharp surface where nonlocal effects are included under the assumption of specular reflection of electrons at the boundary. Their formula may be written[15]

$$r_p=(q_z-I)/(q_z+I)\,, \tag{5a}$$

where

$$I=\frac{i}{\pi}\int_{-\infty}^{\infty}\frac{dq_z'}{q^2}\left(\frac{Q^2}{\epsilon_l(\vec{q},\omega)}+\frac{q_z'^2}{\epsilon_t(\vec{q},\omega)-q^2c^2/\omega^2}\right), \tag{5b}$$

and $\epsilon_l(\vec{q},\omega)$ and $\epsilon_t(\vec{q},\omega)$ are the longitudinal and transverse dielectric functions of the metal, respectively, with $\vec{q}=(\vec{Q},q_z')$. Either of the criteria $r_p(q_z)\to\infty$ or $r_p(-q_z)=0$ now leads to the condition, for $Q>\omega/c$,

$$-i(Q^2-\omega^2/c^2)^{1/2}=I\,. \tag{6}$$

This is precisely the SP dispersion relation derived by Fuchs and Kliewer in a later paper.[16]

Another expression for r_p for a step-density model, which is of slightly less generality than the KF expression, is the one given by Melnyk and Harrison (MH)[17]. Application of our criterion to their formula leads to the SP dispersion relation in the form

$$-\epsilon(\omega)(Q^2-\omega^2/c^2)^{1/2}=[Q^2-\epsilon(\omega)\omega^2/c^2]^{1/2}-Q^2\times[1-\epsilon(\omega)]/(Q^2-K_L^2)^{1/2}\,, \tag{7}$$

where K_L is the solution of $\epsilon_l(K_L,\omega)=0$. It is interesting to note that Eq. (7) follows from Eq. (6) if we choose $\epsilon_t(\vec{q},\omega)=1-\omega_p^2/\omega^2$, and further assume that $\epsilon_l(\vec{q},\omega)$ and K_L^2 are given by their hydrodynamic expressions. Also the dispersion relation obtained by Sauter[6] can be derived as a special case of Eq. (7). Finally, for all cases of reflectance considered so far, one can define a sharp surface separating the metal from vacuum, and we have $r_p(-q_z)=1/r_p(q_z)$.

Of greater interest is to consider the effect of a continuous electronic density profile on the reflectivity of a metal—a problem that has been investigated only recently. Feibelman[8] has derived an expression for r_p from a microscopic theory, which is exact up to terms linear in q_z, by correctly taking into account the changes in the response functions due to a smooth profile. Bagchi and Rajagopal[9] have derived a similar result[18] using a perturbative approach; their expression is more convenient for our purpose, and may be written as

$$r_p(q_z)=r_p^F\left[1-\frac{2iq_z}{(1-\epsilon)(Q^2-\epsilon q_z^2)}\times\left(k_z^2\int_{-\infty}^{\infty}dz\,[\langle\epsilon_{xx}(z)\rangle-\epsilon(z)]+\epsilon^2Q^2\int_{-\infty}^{\infty}dz\,[\langle\epsilon_{zz}^{-1}(z)\rangle-\epsilon^{-1}(z)]\right)\right]\,, \tag{8}$$

where

$$\epsilon=\epsilon(\omega),\quad \epsilon(z)=\Theta(-z)+\epsilon\,\Theta(z)\,,$$

$$\epsilon^{-1}(z)=\Theta(-z)+\epsilon^{-1}\Theta(z)\,,$$

$$\langle\epsilon_{xx}(z)\rangle=\int\epsilon_{xx}(z,z')\,dz'\,,$$

with a similar meaning for $\langle\epsilon_{zz}^{-1}(z)\rangle$. ϵ_{xx} and ϵ_{zz}^{-1} are xx and zz diagonal terms of the corresponding nonlocal dielectric tensors. The metal is assumed to be on the right-hand side ($z>0$), $\Theta(z)$ is the usual step function, and the result is independent of the choice of origin. Here r_p^F is the Fresnel expression for reflectivity. Since this result involves a power-series expansion of the correction term in powers of q_z, it does not appear in the form given by Eq. (4), and we can no longer get the SP dispersion from $r_p(q_z) \to \infty$ criterion. However, we can still get the SP dispersion relation from the condition $r_p(-q_z) = 0$, and this will be a very general dispersion relation in the sense that it would include *all* the effects associated with the surface diffuseness from a microscopic point of view, exactly up to first order in q_z. If we set $r_p(-q_z) = 0$ in Eq. (8), the expression within the large square brackets vanishes since $r_p^F(-q_z)$ can no longer be zero because of the nonlocal effects. For the sake of simplicity, we will take the origin to be at the edge of the jellium background and use the RPA in ϵ_{xx}. Then it is easily shown, by taking the RPA expression[19] for $\sigma_{xx}(z,z')$ and using the charge-neutrality condition, that

$$\lim_{Q\to 0} \int_{-\infty}^{\infty} dz\, [\langle \epsilon_{xx}(z)\rangle - \epsilon(z)] = 0\,. \tag{9}$$

The second integral involving ϵ^{-1} is more difficult to evaluate, and in fact, we do not even know of any simple expression for the nonlocal function $\epsilon_{zz}^{-1}(z,z')$. In absence of this knowledge, we will simply write the second integral

$$\lim_{Q\to 0} \int_{-\infty}^{\infty} dz\, [\langle \epsilon_{zz}^{-1}(z)\rangle - \epsilon^{-1}(z)] = (1/\epsilon - 1)\Delta(Q=0,\omega)\,, \tag{10}$$

where $\Delta(Q,\omega)$ is an unknown function. The $r_p(-q_z) = 0$ condition then gives the SP dispersion relation as

$$\frac{2(Q^2 - \omega^2/c^2)^{1/2}\epsilon Q^2 \Delta(\omega)}{Q^2 + \epsilon(Q^2 - \omega^2/c^2)} = 1\,. \tag{11}$$

If $\Delta = 0$, Eq. (11) reduces to Eq. (1) as it should, and the entire effect of the diffuseness of the surface comes from Δ. We emphasize that Δ also includes the longitudinal response, i.e., Melnyk-Harrison-type corrections, because $\epsilon_{zz}^{-1}(z,z')$ is not a purely transverse response function.[20] To confirm this point we will derive the Harris-Griffin result[10] from Eq. (11). Equation (11) gives in the $c \to \infty$ limit, if we use $\epsilon(\omega) = 1 - (\omega_p/\omega)^2$,

$$\omega^2 = \tfrac{1}{2}\omega_p^2(1 - \Delta Q) + O(Q^2)\,. \tag{12}$$

Now, following Feibelman[8] and using his notation, we can represent the charge-density fluctuation in the system as

$$\delta n(z,Q,\omega) = -\frac{i\omega}{4\pi c}\left(i\vec{Q} + \hat{z}\frac{d}{dz}\right)\cdot \vec{A}_{Q,\omega}(z)\,,$$

which gives

$$\lim_{Q\to 0} \frac{\int z\,\delta n(z,Q,\omega)\,dz}{\int \delta n(z,Q,\omega)\,dz} = \frac{1}{1-\epsilon}\int z\frac{d\mathcal{A}_\omega}{dz}dz\,. \tag{13}$$

But it is easy to show[18] that

$$\int z\frac{d\mathcal{A}_\omega}{dz}dz = -\epsilon\int [\langle \epsilon_{zz}^{-1}(z)\rangle - \epsilon^{-1}(z)]\,dz = -(1-\epsilon)\Delta\,.$$

Hence, the right-hand side of Eq. (13) is equal to $-\Delta$, and Eq. (12) then becomes equivalent to the Harris-Griffin result.[10] So our dispersion relation, Eq. (11), has the correct behavior even in the nonretardation regime for any arbitrary model of the surface.

Let us go back to Eq. (11) and point out that this is a completely new result and is the first SP dispersion relation in the retarded region which takes into account the surface diffuseness in an exact microscopic way. A numerical evaluation of the dispersion relation is not possible, however, because we do not know the frequency dependence of $\Delta(\omega)$ and Δ is a complex quantity. If we assume Δ to be real, independent of ω, and of order $1/k_F$, Eq. (11) gives a dispersion relation which is not too different from Eq. (1), and in particular, it does not yield any additional "higher" modes which have been predicted in the hydrodynamic theories.[21,22] Also note that since Δ is, in general, complex, Q will have an imaginary part even if $\epsilon(\omega)$ is real. Physically this means that Eq. (11) allows for the Landau damping through single-particle excitations.

A realistic calculation of the function $\Delta(Q,\omega)$ is of prime interest for further investigations in this area. Since an exact calculation, even within the RPA, is difficult, an approximate expression based on the sum rules[23] may be useful.

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