Hydrodynamic models of surface plasmons

C. Schwartz and W. L. Schaich
Physics Department, Swain West, Indiana University, Bloomington, Indiana 47405
(Received 26 July 1982)

Hydrodynamic models of surface plasmons on clean metal surfaces are studied for various choices of additional boundary conditions and of equilibrium electron density profile. Both intrinsic and correctable defects of an approach based on hydrodynamics are illustrated. We conclude that for a clean metal surface, a hydrodynamic model of surface plasmons should only be used with considerable caution.

In a recent paper[1] we studied the dispersion and external coupling of phonons at metal surfaces. Our theoretical approach was based on hydrodynamic equations and required at an abrupt surface the imposition of additional boundary conditions ABC's. We found that the derived results depend sensitively on the choice of ABC's and that the only satisfactory choice in the phonon energy range was that at a free surface, zero stress act on both the electrons and the ions. This ABC is the usual one of continuum elasticity theory[2] for atom motion, but it has not been applied before to electrons, where the usual choice is that of zero normal current.

The initial aim[3] of this note was to examine the implications of this new ABC for electrons at plasmon frequencies, where the ion motion is negligible. As we describe below, the results at the simplest level are encouraging but there are definite anomalies; i.e., qualitative disagreements with experiments. When we make systematic improvements in the model some of these anomalies are removed, but new ones also appear. We finally are led to conclude that an approach to surface plasmon oscillations at a clean metal surface using hydrodynamic equations and any ABC is not quantitatively trustworthy and is often even qualitatively wrong. The continued use of such an approach requires at the least that one be aware of its intrinsic defects. We shall briefly illustrate these here. A similar criticism of the hydrodynamic model has been recently published by Ahlqvist and Apell.[4]

Our basic method of calculation is the same as before[1] except that we omit all reference to the ions. The electrons in the metal are described by the hydrodynamic equation

$$\frac{\partial \vec{j}}{\partial t}=f\left(\frac{\omega_p^2}{4\pi}\right)\vec{E}-\beta^2\vec{\nabla}\delta\rho \ , \tag{1}$$

where the induced current $\vec{j}$ and density fluctuation $\delta\rho$ are related by the equation of continuity,

$$\frac{\partial}{\partial t}\delta\rho+\vec{\nabla}\cdot\vec{j}=0 \ ; \tag{2}$$

while the (longitudinal) electric field $\vec{E}$ is determined by Poisson's equation,

$$\vec{\nabla}\cdot\vec{E}=4\pi\delta\rho \ . \tag{3}$$

The phenomenological parameters in (1) are the plasma frequency of bulk metal, ω_p, and the spatial dispersion parameter β. The dimensionless function f describes the one-dimensional variation of the equilibrium electron density through the surface region.

By adopting (1)−(3) as our basic equations we have already dodged several questions of quantitative, but not generally qualitative, importance for the application of the hydrodynamic model. We mention these points here for completeness and have in fact investigated their numerical consequences[3,5]; but for the sake of simplicity we will omit them in this paper. The first is that we work in the electrostatic limit, assuming in effect that the speed of light is infinite. Second, we ignore any damping, either of the Ohmic or Landau type. The former is omitted for simplicity; the latter is beyond the scope of the hydrodynamic model. Third, we assume that a linearized treatment is sufficient and further we neglect the effect of zero-order terms in (1). Thus the possibility of an equilibrium electric field influencing (1) is ignored.[6] Fourth, the spatial dispersion is described by a single number, β, and we shall not even assign it a value. Instead we use the screening wave vector, $k_s=\omega_p/\beta$, as a scale factor. This avoids the ambiguity about the value of β,[7] its possible frequency[8,9] and/or spatial variation.[10] The latter possibility also raises the question of the proper functional form of the last term in (1). For example, if β is position dependent, on which side of the gradient should it appear or is there a more general expression for the pressure term?[4,11,12] We ignore these dilemmas here by representing the electron pressure (stress) simply by $\beta^2\delta\rho$ with β constant, even though f varies.

Our method of solving (1)−(3) is either that of Boardman *et al.*[13] when f has a stepwise variation or that of Bennett[6] when f varies smoothly. In either case one seeks at fixed frequency ω and parallel wave vector $\vec{Q}$ eigenmodes that are localized at the surface. After reducing (1)–(3) to a fourth-order differential equation[6] for ϕ, the electrostatic potential, we either write down[1,13] or numerically generate[6] the several independent partial-wave solutions whose relative coefficients are determined by boundary conditions at points of discontinuity or vanishing of f. Two of the boundary conditions are standard: (1) that ϕ is continuous and (2) that the normal component of the electric displacement field is continuous.[1] However with β finite ABC's are also required. When f is finite on both sides of an interface we require continuity of $\beta^2\delta\rho$ and $\hat{x}\cdot\vec{j}/f$, where $\hat{x}$ is the surface normal. Thus the electron stress and the normal component of the electron displacement are continuous. These two together are consistent with conservation of energy through the interface,[1,14] and are the usual ABC's of plasma physics[15] or elasticity theory.[2] They are not the ABC's of Forstmann and Stenschke,[10] as discussed earlier.[1,14] At the one interface where f finally becomes zero, only a single ABC is mathematically required. We study the consequences of choosing on the material side of the interface either

$$\beta^2\delta\rho=0\ , \tag{4}$$

which we call the stress ABC, or

$$\hat{x}\cdot\vec{j}=0\ , \tag{5}$$

which we call the current ABC. Rather than repeat the possible physical justification for these choices,[1] we illustrate their effect in several model calculations.

These results are shown in Fig. 1 for the stress ABC and in Fig. 2 for the current ABC. In each figure four different choices for f are studied. The f variation versus normal coordinate x is shown in the first column. The diffuseness parameter a is determined by $k_s a=2$. In the middle column we show the dispersion of the surface modes that lie below the bulk plasmons, whose lower bound is $\omega^2=\omega_p^2+\beta^2Q^2$ as indicated by the dashed curve. Finally the third column exhibits the smooth part of the density fluctuation associated with the eigenmode whose frequency tends to $\omega_p/\sqrt{2}$ as $Q\rightarrow 0$. The normalization of the $\delta\rho$ is arbitrary in our linearized theory. In addition there are δ-function contributions to $\delta\rho$ whenever $\hat{x}\cdot\vec{j}$ is discontinuous; i.e., at all discontinuities and the vanishing point of f for the stress ABC and only at $x=0$ in the second row for the current ABC.

Now we discuss the figures from top to bottom, which is in the direction of more realistic choices for f. At the simplest level f drops discontinuously from 1 to 0. For the current ABC, the resulting dispersion which increases linearly at small Q was first derived by Ritchie.[16] The dispersionless result for the stress ABC may be understood as follows. The only partial-wave solution of (1)–(3) that is localized at the surface and that allows a smooth $\delta\rho$ varies as $\exp[i(\vec{Q}\cdot\vec{X}-\omega t)]e^{\bar{Q}x}$, where $\vec{X}$ is parallel to the surface, t is time, and $\bar{Q}^2=Q^2+(\omega_p^2-\omega^2)/\beta^2$. When we require $\beta^2\delta\rho=0$ at $x=0^-$, we force the coefficient of this partial wave to vanish. Indeed the only surviving partial-wave solution in the metal is $\exp[i(\vec{Q}\cdot\vec{X}-\omega t)]e^{Qx}$, which has no β dependence. Hence all the results in the first row of Fig. 1 are the same as if β were zero.

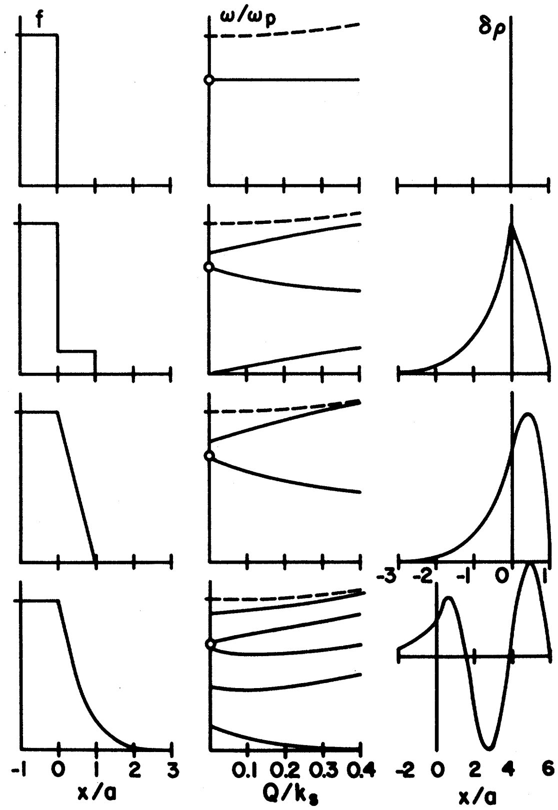

FIG. 1. Hydrodynamic model results under the stress ABC. In the first column is the equilibrium electron density profile; in the second the mode dispersions; and in the third the smooth part of the charge fluctuation of the circled mode to its left. The scales are the same within each column, except for the abscissa in the last row of the last column. See the text for the definition of symbols.

When we compare the dispersion with experimental data, for example,[17] the stress ABC prediction of the first row is a better fit at low Q than the current ABC. Since previous hydrodynamic analyses of surface plasmons used only the current ABC, workers[6,10,13] were forced to give f a less abrupt fall from 1 to 0 in order to obtain an initially flat or decreasing dependence of ω on Q at small Q/k_s.

However the simple stress ABC model of the first row also has a major defect. It predicts no plasmon excitation in this films by p-polarized light. This phenomenon which has been observed in various ways[18,19] is absent theoretically because the stress ABC at both surfaces eliminates $\delta\rho$ (and hence any

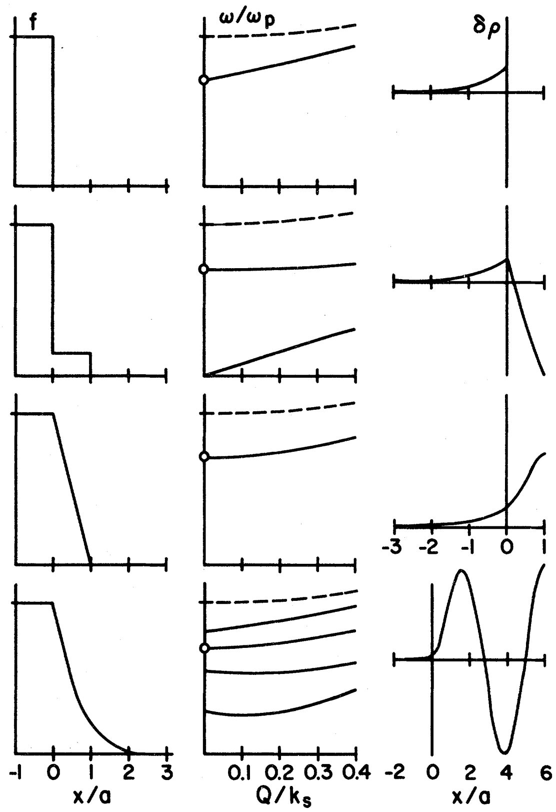

FIG. 2. Hydrodynamic model results under the current ABC, with the same format as in Fig. 1.

plasmon field) inside the film. One must resort to a more sophisticated form of f to correct this defect, or change the ABC.[20] Thus for different reasons with the stress or current ABC's, we consider the remaining rows of the figures.

For all of these cases plasmon excitation in thin films is possible and there are certainly many instances where ω initially decreases with Q. Hence the defects of the first row have been repaired, but at the cost of the general appearance of a multitude of extra modes. These have two discernable origins. First the mode in the second row of both Figs. 1 and 2 that starts from zero is an artifact of the discontinuity of f at $x=0$ interface, and depends only slightly on the ABC at $x=a$. This identification derives from the mode spectrum of an interface between two metals, which corresponds in the second row to letting $a\rightarrow\infty$. One finds[21] then at small Q/k_s the lowest mode varying as $\omega\propto Q^{1/2}$. For finite a, this dependence softens to $\omega\propto Q$ as $Q\rightarrow 0$, analogous to gravity waves in shallow water.[22] When we remove discontinuities in f within the metal, as in the last two rows, this anomalous mode disappears.

The other extra modes are not so easily removed. Indeed, as we allow a more realistic variation of f, they proliferate.[4] These modes are commonly referred to as multipole modes, while the single mode that starts from $\omega_p/\sqrt{2}$ is called the monopole surface plasmon.[12,23] This terminology arises from an analysis of the modes based on moments of $\delta\rho$ and a low Q expansion. Although the analysis was derived for the current ABC it may be readily generalized to the stress ABC,[5] if one also keeps track of the δ-function contributions to $\delta\rho$. We do not present it here but instead offer the interpretation that these extra modes are simply standing plasma waves trapped in the selvedge. This is most clearly seen in the second row case where the condition for the first appearance of a multipole mode at $\omega=\omega_p$ and $Q=0$ is

$$pa=m\pi/2\ , \tag{6}$$

where $p^2=(\omega_p^2-\omega_s^2)/\beta^2$ with ω_s as the "bulk" plasmon frequency of the selvedge. Thus p is the wave vector in the self-edge of a plasmon at $\omega=\omega_p$. The integer m in (6) is even (odd) for the stress (current) ABC. Zero is an even value so at least one multipole mode is always present with the stress ABC, while a critical size of a (i.e., diffuseness) is needed to find the first such mode with current ABC. In the second row of Fig. 2, a multipole mode has just appeared and it only survives over a small Q range.

This qualitative behavior is also apparent in the last two rows where the stress ABC multipole modes are in general more numerous and at lower frequency. For the third row of Fig. 2 a multipole does not appear until $k_s a=2.88$, in qualitative agreement with Bennett's results.[6] It is worth remarking too that the striking difference in the $\delta\rho$ of the monopole mode between the second and third row of Fig. 2 is also a consequence of standing-wave resonance, since roughly a quarter wave is trapped in the selvedge.

This allowance of standing plasmon waves in the selvedge region is a serious flaw of the hydrodynamic model for a clean metal surface.[4] The number of multipole modes and the number of nodes in the monopole $\delta\rho$ depend sensitively on where one finally lets f be zero. In the fourth row f decays exponentially (as $e^{-2x/a}$ for $x>a/2$) out to $x=6a$ where it drops to zero. Extending this cutoff point merely produces more modes and nodes.[24] Allowing β to decrease with x only worsens the situation.[4,5] It seems that the only way to remove this behavior is to include wave-vector–dependent damping, but it is not clear to us how in a hydrodynamic model this introduction of Landau damping may be done in anything less than an *ad hoc* manner. Thus for a clean metal surface it is probably best not to allow f to be too realistic (i.e., to extend too far), with the concomitant realization that fitting experimental data to a surface profile such as in the middle two rows gives little insight into either the proper choice of ABC's or the true shape of f. The situation is better if one is dealing with metal layers, where standing-wave plasmons have been found both in more sophisticated theories[25] and in experiments.[18,19] It is just when the overlayer corresponds to the intrinsic diffuseness of a free-metal surface that the hydrodynamic predictions become quite dubious.

ACKNOWLEDGMENTS

We are grateful to Dr. A. D. Boardman for sending us an excerpt from Ref. 7. Our work was supported in part by the NSF through Grant No. DMR 81-15705.

---

[1]W. L. Schaich and C. Schwartz, Phys. Rev. B 25, 7365 (1982).

[2]L. D. Landau and E. M. Lifshitz, *Theory of Elasticity* (Pergamon, New York, 1970).

[3]C. Schwartz and W. L. Schaich, Bull. Am. Phys. Soc. 27, 343 (1982).

[4]P. Ahlqvist and P. Apell, Phys. Scr. 25, 587 (1982).

[5]C. Schwartz and W. L. Schaich (unpublished).

[6]A. J. Bennett, Phys. Rev. B 1, 203 (1970).

[7]A. D. Boardman, in *Electromagnetic Surface Modes,* edited by A. D. Boardman (Wiley, London, 1982).

[8]J. Harris, Phys. Rev. B 4, 1022 (1971).

[9]L. Kleinman, Phys. Rev. B 7, 2288 (1973).

[10]F. Forstmann and H. Stenschke, Phys. Rev. B 17, 1489 (1978).

[11]G. Mukhopadhyay, Nucl. Solid State Phys. (India) 22C, 725, 729 (1979).

[12]A. Eguiluz, S. C. Ying, and J. J. Quinn, Phys. Rev. B 11, 2118 (1975).

[13]A. D. Boardman, B. V. Paranjape, and R. Teshima, Surf. Sci. 49, 275 (1975).

[14]A. D. Boardman and R. Ruppin, Surf. Sci. 112, 153 (1981).

[15]A. H. Kritz and D. Mintzer, Phys. Rev. 117, 382 (1960).

[16]R. H. Ritchie, Prog. Theor. Phys. 29, 607 (1963).

[17]K. J. Krane and H. Raether, Phys. Rev. Lett. 37, 1355 (1976).

[18]I. Lindau and P. O. Nilsson, Phys. Lett. 31A, 352 (1970); Phys. Scr. 3, 87 (1971).

[19]M. Anderegg, B. Feuerbacher, and B. Fitton, Phys. Rev. Lett. 27, 1565 (1971).

[20]A. D. Boardman and M. R. Parker, Phys. Status Solidi (b) 71, 329 (1975).

[21]This mode is not mentioned by Boardman and Ruppin (Ref. 14), but it is implicit in their equations.

[22]L. M. Milne-Thomson, *Theoretical Hydrodynamics* (Macmillan, New York, 1956).

[23]A. Equiluz and J. J. Quinn, Phys. Lett. 53A, 151 (1973); Phys. Rev. B 14, 1347 (1976).

[24]For the last row, an extra mode occurs when the cutoff distance increases by $\Delta x \sim \pi/k_s$, while an extra node in the $Q=0$ monopole $\delta\rho$ occurs every $\Delta x \sim \pi/(k_s/\sqrt{2})$.

[25]J. E. Inglesfield and E. Wikborg, J. Phys. F 5, 1706 (1975).