Response to a second comment by Conwell on dispersion of surface plasmons in inhomogeneous media

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We answer the criticism in the preceding comment by showing that our formal solutions are correct and argue against the interpretation of our surface-plasmon data in terms of "guided waves."

The mathematical problem and solutions in question have been stated elsewhere[1-8] and need not be repeated here. We note that in Ref. 3, Eq. (8), there is a misprint[9] which should be readily spotted by the interested reader: h_2 is the coefficient of η^3, there is no η^2 term in $U_a(\eta)$.

There are two major points of criticism which the preceding comment directs at Ref. 3. First, it is asserted that the series for $U_a(\eta)$ is incorrect by virtue of errors in the expansion coefficients. Second, it is pointed out that both expansions $U_a(\eta)$ and $U_b(\eta)$ diverge as distance into the bulk increases (i.e., $z \to \infty$). Because of these objections, it is concluded that the second-branch dispersion obtained in Ref. 3 is invalid.

We have reexamined the details of our calculations (Refs. 1 and 3) as well as those of Ref. 5. We find that the formal power-series solutions to Eq. (2)(Ref. 3) [or Eq. (2.7)(Ref. 5)] are correct in both cases. That this is indeed so can be verified directly by substituting $U_a(\eta)$ into Eq. (2),[3] and $F_b(y)$ into Eq. (2.7),[5] to show that the coefficients of powers of η and y vanish. We have checked $U_a(\eta)$ to fourth order, and $F_b(y)$ to second order, and find this to be so. At the risk of seriously belaboring the point, we describe in detail the solution of Eq. (2)(Ref. 3) in the Appendix in the hope of setting at least one question to rest.

Furthermore, since (U_a, U_b) and (F_b, F_a) are each linearly independent solutions of the same equation, U_a must be expressible as a linear combination of F_b and F_a and vice versa.[6] Indeed, we find the following relationship between the two sets of solutions:

$$F_a = U_b,$$
$$F_b = \tfrac{1}{2}(q+\alpha^2)U_a - \tfrac{1}{4}(q+\alpha^2-4\alpha)U_b. \tag{1}$$

Equation (1) can easily be verified using the coefficients listed in Ref. 5 [Eqs. (3.16) and (3.18)] and the coefficients given in Ref. 3, more of which are listed in the Appendix.

In considering the convergence of our series solutions U_a and U_b when $z \to \infty$ (deep into the bulk) we find that these diverge no faster than a geometric series, as do the equivalent solutions (3.14) and (3.15) of Ref. 5. Although strictly, the series diverge only in the limit $z \to \infty$, divergence is already apparent when $z \sim 10a$. For practical purposes the series converge only in the surface region $0 \leqslant z \lesssim 5a$. Within these bounds we obtain a first-order correction due to the assumed inhomogeneity in the electron concentration at the metal surface by truncating the series expansion after the first term. (Solutions which converge rapidly for $0 \leqslant z \leqslant \infty$ are described in detail in Ref. 1. These, however, have undesirable properties for frequencies greater than the surface plasma frequency ω_{ps}. In particular, when $\omega > \omega_{ps}$ these diverge for $0 \leqslant z \lesssim a$ but still converge for $a \lesssim z \leqslant \infty$).

That we may truncate the series for U_a and U_b near the surface is clear since η is small ($\eta \approx 0.2$ at $z=0$)[3] and convergence is rapid; fields are then sufficiently well approximated by retaining just the first term. The dispersion relation is obtained by imposing the usual requirements of continuity on the electric and magnetic fields at $z=0$.[1-3]

In our treatment we reject formal solution $U_a(\eta)$ in the limit of no damping since then $\eta<0$ in frequency domains of interest, as shown in Table I, and for real η, $\ln\eta$ is undefined. Note that for an accumulation layer ($g>0$) the region $\omega < \omega_{pb}$ includes the entire lower branch (branch I of Ref. 1) of the dispersion curve. The region $\omega > (1+g)^{1/2}\omega_{pb}$ encompasses the domain where the second branch (branch II) is expected to lie. For a depletion layer ($g<0$), although $\omega > \omega_{pb}$ is outside the domain of surface-plasmon dispersion, the region $\omega < (1-|g|)^{1/2}\omega_{pb}$ includes the domain in which all of branch I lies, and possibly a portion of the domain in which branch II lies.

Finally we comment on the alternate interpretation offered in the preceding paper for the data reported in Ref. 4. The "guided wave" concept, as introduced in Ref. 7, is based on an equation which is not applicable to either the problem we have considered or to the data presented in Ref. 4. It is not possible to drop derivatives of $\epsilon(\omega, z)$ from a differential equation of the form

TABLE I. Frequency domains where $\eta < 0$ for a depletion or accumulation surface layer. ω_{pb} is the bulk plasma frequency, $\omega_{ps} = (1+g)^{1/2}\omega_{pb}$ is the plasma frequency at $z = 0$.

	$\eta < 0$	$\eta > 0$
$g < 0$	$\omega > \omega_{pb}$ $\omega < (1+\lvert g \rvert)^{1/2}\omega_{pb}$	$\omega_{ps} < \omega < \omega_{pb}$
$g > 0$	$\omega < \omega_{pb}$ $\omega > (1+g)^{1/2}\omega_{pb}$	$\omega_{ps} > \omega > \omega_{pb}$

$$\frac{d^2 H_y}{dz^2} - \left(\frac{1}{\epsilon}\frac{d\epsilon}{dz}\right)\frac{dH_y}{dz} - \kappa^2(z) H_y = 0, \quad (2)$$

without seriously distorting the structure of the equation. If this is done the equation becomes

$$\frac{1}{\epsilon(z)}\frac{d^2 H_y}{dz^2} - \frac{\kappa^2(z)}{\epsilon(z)} H_y(z) = 0, \quad (3)$$

which has solutions

$$H_y(z) = Ae^{\kappa z} + Be^{-\kappa z}, \quad (4)$$

with A and B arbitrary constants. In contrast, if no terms are dropped, Eq. (2) has solutions

$$H_y(z) = e^{-\kappa_b z}[AP_1(z) + BP_2(z)], \quad (5)$$

with $P_1(z)$, $P_2(z)$ the series expansions discussed at the beginning of this response. At best one can expect (4) to be an acceptable approximation to (5) in the limit that $\epsilon(z)$ is a slowly varying function of z. When $\epsilon(z)$ varies exponentially on a scale small compared with the wavelength of the electromagnetic field, this condition is not met. The guided wave concept may indeed have merit for the description of semiconductors with accumulation or depletion layers a few μm thick, but we doubt it is of any use at metallic surfaces for which the scale length of the inhomogeneity is more like 10 or 50 Å. Moreover, the conditions stated in Ref. 7 for the existence of guided waves are not satisfied in our experiments. To wit, it is required that $\epsilon_b(z, \omega) > 0$, which is equivalent to $\omega > \omega_{pb}$ in the free-electron limit, and that $\epsilon_b(z, \omega)$ decrease with distance below the surface, which corresponds to an accumulation layer. In our experiments on Cs-Hg there is a *depletion* layer, and the observed second branch lies *entirely below* ω_{pb}. Thus $\epsilon_b(\omega) < 0$ along the entire branch we observe, and the guided wave interpretation is not tenable.

In a second publication on guided modes, Conwell and Kao approach the solution of Eq. (2) differently.[8] It is pointed out by them that when $\epsilon(z, \omega)$ is real, there exists a range of frequencies for which $\epsilon(z, \omega) = 0$ at some point $z_0(\omega)$, where $z_0(\omega) = a \ln[(\omega_{pb}^2 - \omega^2)/(\omega_{pb}^2 - \omega_{ps}^2)]$. Solutions of Eq. (6) of Ref. 8 [or equivalently, Eq. (2) of Ref. 3] are then sought by expanding about the singular point $z_0(\omega)$.

It should be pointed out, first of all, that $z_0(\omega)$ is an irregular singular point of Eq. (6) of Ref. 8, which, by the way, is misprinted and should read

$$\frac{d^2 G}{dz^2} - \left(\frac{1}{\epsilon}\frac{d\epsilon}{dz}\right)\frac{dG}{dz} + \left(P_0^2 - \frac{\omega^2}{C^2}\,\Delta\epsilon\, e^{z/a}\right)G = 0. \quad (6)$$

Because $z_0(\omega)$ is irregular, a nontrivial regular solution may or may not exist at $z = z_0$ and the details of the solution become important.

Second, for the depletion layer considered in Ref. 8, when $\omega < \omega_{ps}$, $z_0 > 0$ (i.e., outside the conducting medium).[10] Clearly Eq. (6)(Ref. 8) is not applicable when $z > 0$, which is the dielectric half space. In addition, when $\omega > \omega_{pb}$, z_0 has no meaning as the argument of the logarithm becomes negative. In Fig. 1 of Ref. 8, however, continuous guided mode dispersion curves are shown to be uneffected when passing through $\omega = \omega_{pb}$. In short, solutions of Eq. (6)(Ref. 8) expanded about $z_0(\omega)$, if these exist and are nontrivial, can only be valid in the region $\omega_{ps} < \omega < \omega_{pb}$.

Finally, when damping is introduced into the problem, no matter how small, $\epsilon(\omega, z)$ will no longer be zero at some set of points $z_0(\omega)$ and this particular singularity is removed from the problem.

It is clear that the guided mode concept introduced in Ref. 8 is not applicable to the Cs-Hg case we have studied.

In Ref. 1 we obtained an exact description of the surface-plasmon dispersion at a metal surface overlaid with a thin film of a different metal (discontinuous boundary case). In Refs. 1, 2, and 3 the dissimilar metal boundary was removed by adopting the exponential dielectric function model described above and approximate dispersion relations were obtained. These reduced properly to the exact results for the discontinuous boundary case. A second dispersion branch is predicted for *both* discontinuous boundary model and exponential dielectric function model—and the two forms, one exact and one approximate, are seen to be closely related. Specifically, they agree with respect to (i) slopes of the depletion and accumulation layer dispersion curves, (ii) dependence on the degree of inhomogeneity g, (iii) dependence on the scale length of the inhomogeneity a, and (iv) frequency limits outside of which the second branch does not exist. The dispersion curve we have observed and reported in Ref. 4 falls within the theoretical frequency bounds, is consistent with $0.1 \leq g \leq 0.3$ as expected, and indicates that there is a depletion layer at the surface of liquid Hg-Cs, as is required by thermodynamic arguments. We see no validity in the proposed reinterpretation of these experimental observations.

We trust that the last suggestion in the preceding comment about our observations, namely, that in 30% Cs-Hg the Cs lies atop the Hg and that there is a discontinuous change in $\epsilon(z)$ as distance into the bulk increases (so that this system is like a thin film atop a metal), will be seen to be nonsense. *We have studied a liquid, with mobile ions.* How could one develop a discontinuous boundary between pure Cs and Cs-Hg in a *one-phase* liquid system? Given the high mobility of the ions, and the fact that solutions are stable (one-phase system) diffusion will remove sharp (one atomic diameter) boundaries. The scale length of the inhomogeneity might not be large but surely no one expects there to be a discontinuous boundary between two mutually soluble species in a one-phase fluid system.

In conclusion, we have answered all of the critical remarks in the preceding paper in some detail. We have shown that our formal solutions of Eq. (2)(Ref. 3) are not in error, that both these and the formal solutions of Ref. 5 do indeed satisfy Eq. (2).[3] We have obtained a relationship between the two sets of solutions, and have shown them to be equivalent. We have answered the suggestion that the data in Ref. 4 could be reinterpreted in terms of guided modes, and we have commented on the thermodynamics of miscible fluids and argued against discontinuous fluid separation in such a mixture.

APPENDIX

Solutions of

$$\eta(\eta+1)\frac{d^2U}{d\eta^2}+(z\alpha\eta-1)\frac{dU}{d\eta}-(\alpha+q\eta)U=0 \quad \text{(A1)}$$

may be expanded about the regular singular point $\eta=0$. The indical equation then has roots 0 and 2, and solutions are of the form

$$U_1=\sum_{n=0}^{\infty} a_n\eta^{n+2}, \quad \text{(A2a)}$$

$$U_2=\sum_{n=0}^{\infty} b_n\eta^{n}+CU_1\ln\eta, \quad \text{(A2b)}$$

where C is an arbitrary constant. The coefficients a_n and b_n are obtained by direct substitution into Eq. (A1). A recusion relation for a_n is

$$(n+3)(n+1)a_{n+1}+[(n+2)(n+1)+2\alpha(n+2)-\alpha]a_n -qa_{n-1}=0, \quad n\geq 1, \quad \text{(A3)}$$

with a_0 arbitrary and $a_1=-\frac{1}{3}(2+3\alpha)a_0$.

The coefficients b_n are obtained from

$$Ca_n[2\alpha+(2n+3)]+2a_{n+1}(n+2)C-qb_{n+1} +b_{n+2}[(3+2n)\alpha+(n+1)(n+2)] +b_{n+3}(n+1)(n+3)=0, \quad n\geq 0, \quad \text{(A4)}$$

with

$$b_0=Ca_0/\tfrac{1}{2}(q+\alpha^2), \quad b_1=-\alpha b_0, \quad b_2 \text{ arbitrary}.$$

Note that each b_n for $n\geq 3$ can be separated into two parts; one that depends on a_0 and one that depends on b_2. Separation generates, respectively, the new coefficients h_n and $f_n=a_n/a_0$ in terms of which U_2 is rewritten

$$U_2=Ca_0U_a+b_2U_b, \quad \text{(A5)}$$

where

$$U_a=U_b\ln\eta+h_0+h_1\eta+h_2\eta^3+h_3\eta^4+\cdots =U_b\ln\eta+h_0+h_1\eta+\eta\sum_{n=z}^{\infty}h_n\eta^n, \quad \text{(A6)}$$

$$U_b=\eta^2+f_1\eta^3+f_2\eta^4+\cdots =\eta^2\sum_{n=1}^{\infty}f_n\eta^n. \quad \text{(A7)}$$

Therefore, U_2 is the general solution.

That U_a is indeed a solution of Eq. (A1) is verified by direct substitution. We obtain, to fourth order,

$$-(h_1+\alpha h_0)\eta^0+(2+\alpha h_1-qh_0)\eta^1 +(3+4\bar{a}_1+2\alpha+3h_2-qh_1)\eta^2 +[6\bar{a}_2+(5+2\alpha)\bar{a}_1+(5\alpha+6)h_2+8h_3]\eta^3 +[(12+7\alpha)h_3+15h_4-qh_2 +(7+2\alpha)\bar{a}_2+8\bar{a}_3]\eta^4+\cdots=0. \quad \text{(A8)}$$

The coefficient of each power of η is identically zero and U_a therefore satisfies the differential equation. Given Eq. (1) it follows that F_b is a solution of Eq. (A1) since U_b is also.

A few additional coefficients are listed explicitly below for convenience:

$$a_2=a_0[\tfrac{1}{24}(6+5\alpha)(2+3\alpha)+\tfrac{1}{8}q],$$
$$a_3=-\tfrac{1}{360}a_0[(12+7\alpha)(6+5\alpha)(2+3\alpha)+q(52+45\alpha)]; \quad \text{(A9)}$$

$$-3b_3=ca_0[(\tfrac{1}{3}-2\alpha)+2\alpha q/(q+\alpha^2)+(2+3\alpha)b_2,$$
$$-8b_4=c[a_1(5+2\alpha)+6a_2]+(5\alpha+6)b_3-qb_2, \quad \text{(A10)}$$
$$-15b_5=c[a_2(2\alpha+7)+8a_3]-qb_3+(7\alpha+12)b_4.$$

From the coefficients b_n we obtain f_n and h_n:

$$f_1 = \bar{a}_1 \equiv a_1/a_0\,,\quad f_2 = \bar{a}_2 \equiv a_2/a_0\,,\quad \vdots \quad f_n = \bar{a}_n \equiv a_n/a_0\,; \tag{A11}$$

$$\begin{aligned} h_0 &= b_0 = 2/(q+\alpha^2)\,,\\ h_1 &= -\alpha h_0\,,\\ h_2 &= -\tfrac{1}{3}[(\tfrac{1}{3} - 2\alpha) + 2\alpha q/(q+\alpha^2)]\,,\\ -8h_3 &= (5+2\alpha)\,\bar{a}_1 + 6\bar{a}_2 + (5\alpha+6)\,h_2\,,\\ -15h_4 &= (2\alpha+7)\bar{a}_2 + 8\bar{a}_3 - q\,h_2 + (12+7\alpha)\,h_3\,. \end{aligned} \tag{A12}$$

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[7] E. M. Conwell, Solid State Commun. 14, 915 (1974).

[8] E. M. Conwell and C. C. Kao, Opt. Commun. 17, 98 (1976).

[9] This misprint had been communicated to Esther M. Conwell, preceding paper, Phys. Rev. B 18, 5881 (1978).

[10] For the discussion in this paragraph we adopt the convention in Ref. 8 where the conductor is confined to the half space $z < 0$.