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Multipole surface plasmons and photoemission yield spectra

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We demonstrate that in order for hydrodynamic-model calculations to reproduce recent photoemission yield spectra the parameters must be chosen to ensure the existence of an extra surface collective mode below the plasma frequency. Hence, the agreement between these model calculations and the data establishes for the first time the existence of such modes on a smooth clean metal surface.

In a recent paper,[1] Kempa and Forstmann (KF) present a hydrodynamic-model calculation of photoemission yield from Al. Their theoretical curves agree quite well with experimental data,[2,3] the key feature of which is a peak in the yield for photon frequency $\omega \simeq 0.8\omega_p$ followed by a reduced yield at ω_p and beyond, where ω_p is the plasma frequency. Their calculations, however, do not represent the first such success since several previous theoretical works using different models have also been able to predict[4-6] or to reproduce[3,7,8] some features of the data. The calculations by Feibelman[3,5,9] are perhaps the most convincing in that they involve the fewest approximations and attain the most extended agreement with the data. Still his model description omits band-structure effects and bulk absorption processes, which prevents its extension to many materials and its computational complexity makes the extraction of a qualitative picture difficult. These limitations have led several workers to develop simpler models.[1,7,8,10]

From this point of view the results of KF acquire an additional importance since their simple model provides both a good fit to the data and a physical explanation of the peak below ω_p. They attribute this peak in the yield to "starting plasma waves" in the metal's selvedge and argue that the necessary theoretical ingredients for its appearance are a soft electron-density gradient at the surface and the use of nonlocal constitutive relations. The former they model by letting the equilibrium electron density fall to zero in two steps and the latter is included via the linearized hydrodynamic equation of motion for the electrons' response

$$\frac{\partial \vec{j}}{\partial t} = \frac{\omega_p^2}{4\pi}\vec{E} - \beta^2 \vec{\nabla}\,\delta\rho - \vec{j}/\tau \ . \tag{1}$$

Here $\vec{E}$ is the total electric field and $\vec{j}$ ($\delta\rho$) is the induced electron current (charge) density. The local plasma frequency ω_p is proportional to the square root of the local equilibrium density n_0 while the spatial dispersion parameter β scales with $n_0^{1/3}$ and the lifetime τ is presumed constant within the metal. The values of ω_p and β in the bulk, as well as the width L and fractional height f of the density step, are taken from an earlier fit[11] to the surface-plasmon dispersion relation as measured by electron energy-loss experiments:[12]

$$\hbar\omega_p = 15.3 \text{ eV}, \quad \beta = 1.64\times 10^8 \text{ cm/sec} \ ,$$
$$L = 4 \text{ Å}, \quad f = 0.7 \ .$$

The value of τ is chosen so that $\omega_p\tau = 10$. The detailed journey of how one may proceed from (1) to an expression for the photoemission yield is outlined in their paper, so we shall not repeat it. See also the reviews in Refs. 10 and 13.

We note, however, that the path is not unique and that at several points one needs to choose further assumptions. In order to test the numerical significance of alternate choices, we have examined several related versions of the basic hydrodynamic model and discovered a unifying feature that KF did not point out. We agree with KF that one criterion for a significant peak below ω_p to appear is that the electron-density profile not be sharp. In addition to this, however, it is also necessary that the surface support extra collective modes besides the usual surface plasmon. Indeed the photoemission yield peak is centered on the collective mode frequency that may be most efficiently excited. For the rest of this Rapid Communication we expand on these claims.

The possible existence and properties of extra surface collective modes have been most extensively studied by the group at Brown University[14-18] (see also references in Ref. 13), who refer to them for finite β as multipole surface plasmons, where the monopole surface plasmon is the familiar excitation whose (nonretarded) frequency at zero parallel wave vector Q is $\omega_p/\sqrt{2}$. We also include in our study the case of no spatial dispersion, $\beta \equiv 0$, which for a stepped surface density allows more than one surface collective mode, too.[19] None of these bound surface modes directly enter the calculations, rather their "leaky" mode counterparts appear since the perturbing photon field puts one on the radiative side of the light line. More specifically, the surface electric fields are enhanced when the photon frequency passes through such "modes", which are not precisely defined since they may decay by both radiative and nonradiative processes. The enhanced surface fields are, in turn, responsible for the peak in the photoemission yield.

To illustrate this correlation we show in Figs. 1–3 some of our results. The photoemission yield curve is here taken as

$$Y = 1/2 \int_0^\infty dx\, e^{-x/\lambda} \frac{4\pi}{\omega_p^2(x)\tau} |\vec{j}(x)|^2 \ , \tag{2}$$

where the integral runs over the metal and the escape length $\lambda = 10$ Å (Ref. 1). The current density $\vec{j}$ is determined from Eq. (1) and is normalized so that Y represents

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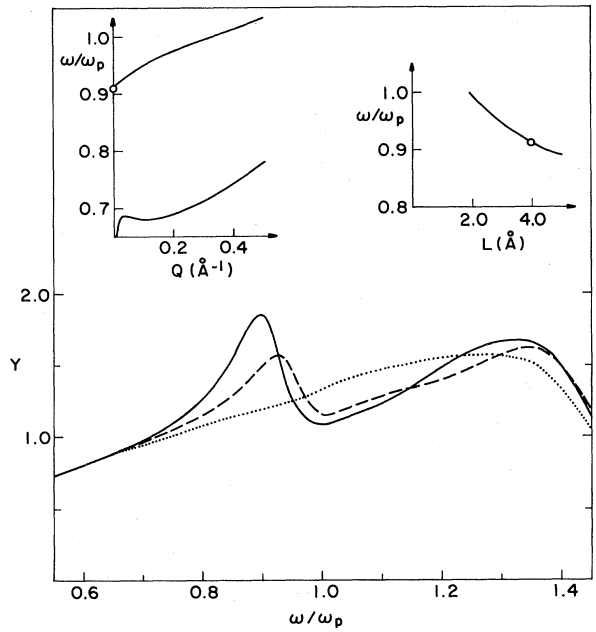

FIG. 1. Photoemission yield per incident photon according to KF's ABC vs photon frequency. The yield is plotted in the same arbitrary units in Figs. 1–3. Curves for various widths of the selvedge are shown: ——, $L=4$ Å; – – –, $L=3$ Å; and · · ·, $L=1.7$ Å. In the upper right inset the $Q=0$, $1/\tau=0$, nonretarded extra surface-mode frequencies are plotted vs L. In the upper left inset the $1/\tau=0$, $L=4$ Å retarded dispersion relation is shown for both the monopole surface plasmon and the multipole surface plasmon. The $Q=0$, nonretarded limit of the latter is denoted by the open circle on both the left and right insets and shows how the right inset is constructed in Figs. 1–3.

the yield per incident photon due to p-polarized light with a 45° angle of incidence. KF show that such a formula provides a reasonable fit to the data for their choice of parameters (curve 9 in their Fig. 5), although they normalized their Y to a unit photon energy flux. In Fig. 1 the calculation is initially done according to their prescription of boundary

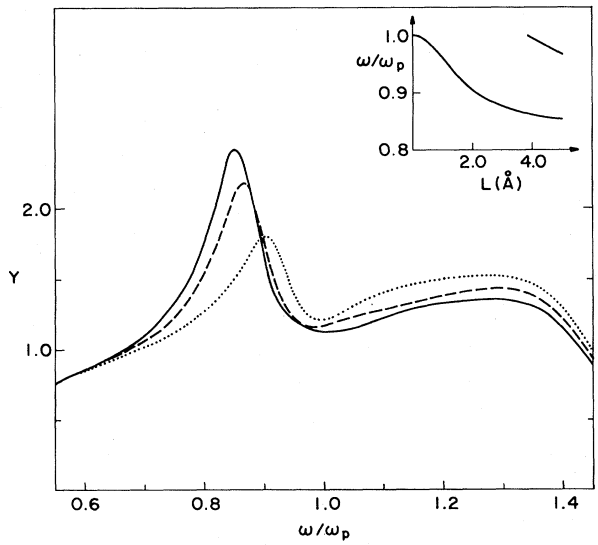

FIG. 2. Photoemission yield per incident photon according to the stress ABC vs photon frequency. Plotting scheme is the same as in Fig. 1.

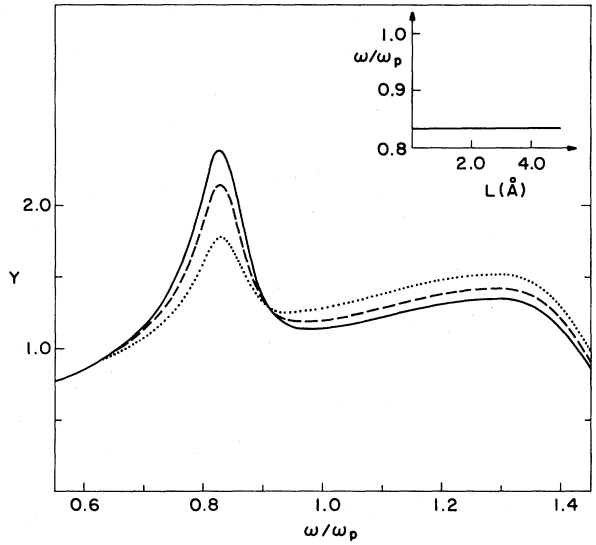

FIG. 3. Photoemission yield per incident photon according to classical optics ($\beta\equiv 0$) vs photon frequency. Plotting scheme is the same as in Fig. 1.

conditions and parameter choices. Then keeping all other parameters fixed, we decrease the width L of the electron-density step down to the value of 1.7 Å below which the extra surface mode can no longer exist in their model, given the other parameter choices.[20] The point to notice is that the peak in the photoemission yield below ω_p disappears when the extra surface mode disappears. Indeed this peak closely tracks the extra surface mode location, whose nonretarded $Q=0$ value is shown in the inset.

This behavior is most apparent in Fig. 2 where the same calculations are done but with a different choice of an additional boundary condition (ABC), what we have called the stress ABC.[20–22] Under this ABC at least one extra surface mode is always present for $L\neq 0$. Note that when a second extra surface mode is allowed, only the lowest one appears in Y. This is a consequence of the large value of $1/\tau$ used here, see Ref. 22 for calculations that exhibit several of these modes simultaneously.

In Fig. 3 again the same calculations are done but now with $\beta\equiv 0$, i.e., the spatial dispersion is removed from the model. There is still an extra surface mode but it does not change location with L, nor does the peak location in Y. The peak height of Y does decrease with shrinking L, however, because the fields are enhanced only in the near vicinity of the step, a feature apparent in all of the figures.

We have found the same general behavior in several further calculations, for example, for the choice of what we call the current ABC.[22,23] If we change the prescription for finding the yield to simply the absolute square of the integral of the normal component of the electric field over a fixed distance down into the metal,[1] the same qualitative results are found in each case although the quantitative curves depend strongly on the choice of the escape depth and the lifetime τ. Yet as long as at least one extra surface mode is present and L is not too small, a clear peak appears in the photoemission yield below ω_p. When there are several extra surface modes, the lowest one produces the strongest structure.

We stress that we are not trying here to improve the agreement between KF's theory and the experimental data, which is reasonably good, but instead are seeking to clarify its interpretation. As noted by KF one may improve the

quality of the fit by slightly modifying all the parameters of the model, but this is of little significance since the final choice of parameters would be different for different choices of ABC or photoemission yield formula. There is at present no fundamental way to choose among these since they are all approximate. The only common features in such an effort would be the need for a soft density gradient, an extra surface mode at the proper frequency, and a suitable choice of τ to mimic the strong particle-hole damping that such modes must be subject to, but which is beyond the scope of the hydrodynamic model to describe *a priori*. Hence, we feel that one should hope for no more from the hydrodynamic model than this qualitative view.

It is of interest, however, to ask whether this rough interpretation can be of use in understanding more sophisticated calculations, which bring us to ask whether photoemission yield spectra can prove the existence of surface collective modes. We should first qualify this question to apply to smooth, clean metal surfaces since it has already been answered in the affirmative for a metal overlayer on an insulating substrate.[24] In addition, there have been several theoretical efforts[25–28] to produce a quantitative understanding of the data. Although these use differing models, there seems to be no question that the structure in the photoemission yield is due to the excitation of standing plasma waves in the overlayer, which may be viewed as an extended selvedge. In contrast for smooth, clean metal surfaces there has been, to the best of our knowledge, no report of an experimental detection of extra surface collective modes. On the theoretical side it is also an open question whether such modes can exist.[20,29–31] If our interpretation of the photoemission yield peak is correct, then these data would provide the first evidence (see also Ref. 32).

The primary counter argument to this proposal is that the peak in the photoemission yield may be explained in different physical terms. For instance, the models used in Refs. 4, 6, and 7 all have an abrupt drop in the electron density at the surface, which precludes the existence of extra surface modes. On the one hand this shows that alternate mechanisms can lead to a peak, but on the other hand their results all seem to produce peaks at photon frequencies too low compared with experiment.

This latter argument cannot be used against the results of Feibelman[3,5,9] or Apell.[8] Feibelman explains his calculation in terms of single-particle matrix element effects due to the changing range with ω of the spatial variation of the surface electric field. These variations, however, have been shown by KF to be well reproduced by the hydrodynamic-model fields and our calculations show that the presence of an extra surface mode is necessary to obtain this agreement. We hence conclude that our explanation is not inconsistent with his and in fact may shed new light on his calculations. For instance, he has computed the photoemission yield to be expected from three systems which differ only in the diffuseness of their equilibrium electron density profiles—see Fig. 2 in Ref. 5. As the surface profile becomes less diffuse the photoemission yield peak moves up towards ω_p, qualitatively, just as a multipole mode would do—see Figs. 1 and 2. This test of further implications may also be applied to the model developed by Apell.[8] In the same limit of sharpening surface gradient, his theory predicts a reduced photoemission yield but no shift of the peak location. Hence, his theory, like that of Fig. 3, misses a significant qualitative feature.

The above arguments lead us to conclude that one may usefully interpret the reported yield peak in photoemission just below ω_p as evidence for the existence of an extra surface collective mode. Although hydrodynamic models cannot give a fundamental description of this structure, they can be readily fit to it. The resulting parameters can then be used to calculate many other surface response properties. For instance, our calculations indicate that the reflectivity should show a few percent dip near the extra surface mode frequency while an external electron energy loss spectrum will show essentially only the monopole surface plasmon loss. It is by correlating these various properties within a common viewpoint that the hydrodynamic approach and its simple interpretation becomes very helpful.

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