Inelastic scattering of x rays by surface plasmons

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A theoretical estimate is made of the scattering efficiency of x rays by surface and bulk plasmons near a flat metal surface. The density-density correlation function needed by the theory is taken from hydrodynamic theory. At grazing angles of incidence and exit, specifically beyond the critical angle, the surface and bulk-plasmon losses can be of comparable strength. An estimate of their absolute magnitude suggests that they should be experimentally detectable if high-intensity x-ray sources are used. Several model calculations are presented to illustrate the possible spectra.

I. INTRODUCTION

The physics of surface plasmons has been an intriguing subject for a long time, and several excellent reviews of previous work are available.[1–6] In this paper we explore the feasibility of a new way to examine the subject. We have in mind inelastic x-ray scattering, which has indeed often been used to study bulk-plasmon dispersion and damping.[7–10] Here, Refs. 7 and 8 are reviews of early work, while Refs. 9 and 10 are examples of recent efforts. However, aside from some interesting studies of the inelastic scattering produced by colloidal graphite particles,[11,12] no one seems to have reported the loss of surface-plasmon quanta by x-rays. There also is, to our knowledge, no explicit estimate of the expected coupling strength when the scattering takes place at a flat metal surface,[2,13] although an estimate has been made for the excitation of surface plasmons on spheres.[14]

Since the interaction between x-rays and matter is relatively weak, and further because the density fluctuations associated with surface plasmons extend, at most, a few tens of angstroms into a metal, one would expect that the net coupling would be quite small. Our calculations confirm this guess, but also provide a definite numerical estimate of its strength and suggest configurations that would enhance its observation. It is our hope that, with the steadily increasing intensities available from synchrotron-radiation sources,[15–17] experimental detection of inelastic x-ray scattering from surface plasmons at a flat metal surface might soon be studied.

The plan of the remainder of this paper is as follows. In Sec. II we develop a phenomenological derivation of the scattering efficiency. The basic quantity required by our theory is the density-density correlation function of mobile electrons near a metal surface. Expressions for this quantity have been recently derived within a hydrodynamic model description of a metal's response[18] and will be used here. In Sec. III we present several model calculations of the scattering efficiency. This numerical work shows the importance of working at grazing angles of incidence and exit in order to enhance the coupling to surface plasmons over bulk plasmons. It also demonstrates how experimental data could help discriminate between various models of surface-plasmon dispersion and damping.

II. DERIVATION

To derive a formula for the efficiency of x-ray scattering from plasmons at a metal surface, we adapt the phenomenological approach used by Mills *et al.*[19–21] to describe Raman scattering by phonons. The limitations of the theory will be described as we develop it.

We imagine that the inelastic x-ray scattering is due to fluctuations in the dielectric response of the metal's electrons. In the absence of such fluctuations, the polarization inside the metal is presumed to be given by the local, isotropic expression

$$\mathbf{P}_0(\mathbf{x},t)=\frac{\epsilon_0(\omega_i)-1}{4\pi}\mathbf{E}_i(\mathbf{x})e^{-i\omega_i t}\ , \tag{1}$$

where $\mathbf{E}_i(\omega_i)$ is the incident x ray's electric field (frequency) and $\epsilon_0(\omega_i)$ is the dielectric function. For a simple Drude model, ϵ_0 would be

$$\epsilon_0(\omega)=1-\omega_p^2/\omega^2\ , \tag{2}$$

where

$$\omega_p^2=4\pi n_0 e^2/m\ , \tag{3}$$

with m, e, and n_0 equal to, respectively, the mass, charge, and equilibrium density of the responding electrons. The only one of these parameters in ϵ_0 that can fluctuate is the density, which we now replace by $n_0+\delta n$, so that $\mathbf{P}_0\rightarrow\mathbf{P}_0+\delta\mathbf{P}$, where

$$\delta\mathbf{P}(\mathbf{x},t)=-\frac{e^2\delta n(\mathbf{x},t)}{m\omega_i^2}\mathbf{E}_i(\mathbf{x})e^{-i\omega_i t}\ . \tag{4}$$

This ansatz for $\delta\mathbf{P}$ is physically reasonable if there is a clear dichotomy between the space-time variations of the modes being occupied. For us this distinction is between x-ray photons and metal plasmons, while for Mills *et al.* an analogous result depends on the difference between visible light and phonons.[19–21]

We introduce a Fourier decomposition of δn in time and in the two space coordinates parallel to the flat surface. Wave and position vectors in this plane are denoted by capital letters with undertildes, while components normal to the surface are written as lower-case letters and carry no tilde. With this notation, the fluctuating polarization field is described by

$$\delta\mathbf{P}(\mathbf{x},t)=-\frac{1}{T}\sum_{\omega}\frac{1}{A}\sum_{\underset{\sim}{Q}}\frac{e^2\delta n(x;-\underset{\sim}{Q},-\omega)}{m\omega_i^2}\times\mathbf{E}_i(x;\underset{\sim}{K}_i,\omega_i)e^{i(\underset{\sim}{K}_s\cdot\underset{\sim}{X}-\omega_s t)}$$

$$=\frac{1}{T}\sum_{\omega}\frac{1}{A}\sum_{\underset{\sim}{Q}}\delta\mathbf{P}(x;\underset{\sim}{K}_s,\omega_s)e^{i(\underset{\sim}{K}_s\cdot\underset{\sim}{X}-\omega_s t)}\,, \tag{5}$$

where $\underset{\sim}{K}_s=\underset{\sim}{K}_i-\underset{\sim}{Q}$, $\omega_s=\omega_i-\omega$, and $A(T)$ is a quantization area (time). We will eventually replace $(1/T)\sum_\omega \to \int(d\omega/2\pi)$ and $(1/A)\sum_{\underset{\sim}{Q}}\to\int[d^2Q/(2\pi)^2]$.

Next, we turn to Maxwell's equations, which under the assumptions of $\mathbf{H}=\mathbf{B}$ and no external sources, appear as

$$\nabla\cdot\mathbf{D}=0,\quad \nabla\cdot\mathbf{B}=0\,,$$
$$\nabla\times\mathbf{E}=-\frac{1}{c}\frac{\partial\mathbf{B}}{\partial t},\quad \nabla\times\mathbf{B}=\frac{1}{c}\frac{\partial\mathbf{D}}{\partial t}\,, \tag{6}$$

where c is the speed of light. We wish to combine these with the constitutive equations (1) and (4) to calculate the scattered electric field $\mathbf{E}_s$ produced by $\delta\mathbf{P}$, with the latter treated as a perturbation. Schematically, we write

$$\mathbf{D}=\epsilon_0\mathbf{E}+4\pi\delta\mathbf{P}\,, \tag{7}$$

and eliminate $\mathbf{B}$ from (6) to find

$$\frac{1}{c^2}\frac{\partial^2}{\partial t^2}\epsilon_0\mathbf{E}-\nabla^2\mathbf{E}=-\nabla(\nabla\cdot\mathbf{E})-\frac{4\pi}{c^2}\frac{\partial^2}{\partial t^2}\delta\mathbf{P}$$
$$=\frac{4\pi}{\epsilon_0}\left[\nabla(\nabla\cdot\delta\mathbf{P})-\frac{\epsilon_0}{c^2}\frac{\partial^2}{\partial t^2}\delta\mathbf{P}\right]. \tag{8}$$

In lowest order the right-hand side of (8) is set to zero. This yields the equation satisfied by the incident electric field, which we treat as a single transversely polarized plane wave within the metal,

$$\mathbf{E}_i(\mathbf{x},t)=\mathbf{E}_i e^{i(\mathbf{k}_i\cdot\mathbf{x}-\omega_i t)}\,, \tag{9}$$

where $\mathbf{k}_i=(-k_i,\underset{\sim}{K}_i)$, satisfying

$$\mathbf{k}_i\cdot\mathbf{E}_i=0\,, \tag{10a}$$

$$\mathbf{k}_i\cdot\mathbf{k}_i=\epsilon_0(\omega_i)(\omega_i^2/c^2)\,, \tag{10b}$$

with ω_i and $\underset{\sim}{K}_i$ real-valued, and the complex-valued k_i chosen to lie in the first quadrant.

At the next order, we consider $\delta\mathbf{P}$ as a known inhomogeneous term that generates $\mathbf{E}_s$. Writing, as in (5),

$$\mathbf{E}_s(\mathbf{x},t)=\frac{1}{T}\sum_{\omega}\frac{1}{A}\sum_{\underset{\sim}{Q}}\mathbf{E}(x;\underset{\sim}{K}_s,\omega_s)e^{i(\underset{\sim}{K}_s\cdot\underset{\sim}{X}-\omega_s t)}\,, \tag{11}$$

a particular solution of

$$\left[\epsilon_0(\omega_s)\frac{\omega_s^2}{c^2}+\nabla^2\right]\mathbf{E}_s$$
$$=-\frac{4\pi}{\epsilon_0(\omega_s)}\left[\nabla(\nabla\cdot\delta\mathbf{P})+\epsilon_0(\omega_s)\frac{\omega_s^2}{c^2}\delta\mathbf{P}\right] \tag{12}$$

is

$$\mathbf{E}_s(x;\underset{\sim}{K}_s,\omega_s)=\frac{2\pi i}{\epsilon_0(\omega_s)k_s}\int dx'\left[(\delta\mathbf{P}'\cdot\nabla)\nabla+\epsilon_0(\omega_s)\frac{\omega_s^2}{c^2}\delta\mathbf{P}'\right]e^{ik_s|x-x'|}\,, \tag{13}$$

where $\delta\mathbf{P}'=\delta\mathbf{P}(x';\underset{\sim}{K}_s,\omega_s)$ and

$$k_s^2=\epsilon_0(\omega_s)\frac{\omega_s^2}{c^2}-K_s^2\,, \tag{14}$$

with the complex k_s again chosen to lie in the first quadrant. If the integration keeps $x'<x$, then $\mathbf{E}_s$ becomes

$$\mathbf{E}_s(x;\underset{\sim}{K}_s,\omega_s)=\frac{2\pi i}{\epsilon_0(\omega_s)k_s}e^{ik_s x}\int_{x'<x}dx'[-\mathbf{k}_s(\mathbf{k}_s\cdot\mathbf{E}_i)+(\mathbf{k}_s\cdot\mathbf{k}_s)\mathbf{E}_i]\left[\frac{-e^2\delta n(x';-\underset{\sim}{Q},-\omega)}{m\omega_i^2}\right]e^{-i(k_s+k_i)x'}$$
$$=\frac{2\pi i}{k_s}\left[\frac{e^2}{mc^2}\right]\left[\frac{\omega_s^2}{\omega_i^2}\right]e^{ik_s x}[\hat{\mathbf{k}}_s\times(\hat{\mathbf{k}}_s\times\mathbf{E}_i)]\delta n(-\mathbf{q},-\omega)\,, \tag{15}$$

where $\hat{\mathbf{k}}_s=\mathbf{k}_s/(\mathbf{k}_s\cdot\mathbf{k}_s)^{1/2}$ is a unit vector, and $\mathbf{q}=(q,\underset{\sim}{Q})$ with

$$q=-(k_i+k_s)\,, \tag{16}$$

so that $\mathrm{Im}q<0$. Now we further replace e^2/mc^2 by r_0 and set $\omega_s^2/\omega_i^2=1$, which must be essentially true if our ansatz for $\delta\mathbf{P}$, Eq. (4), is to be valid. Then,

$$\mathbf{E}_s(x;K_s,\omega_s)\approx\frac{2\pi i r_0}{k_s}e^{ik_s x}[\hat{\mathbf{k}}_s\times(\hat{\mathbf{k}}_s\times\mathbf{E}_i)]\delta n(-\mathbf{q},-\omega)\,. \tag{17}$$

This equation describes the outgoing, inelastically scattered wave amplitude just inside the metal, which lies in $x<0$, in terms of the incident field amplitude that has been refracted into the metal.

There remains the untidy business of relating the outside fields to the inside fields, and of extracting a scattering probability. We shall only outline how one completes these tasks. The first is algebraically the worst. Mills *et al.* use Green's functions to do it,[19–21] but we shall merely note that, by using $\epsilon_0(\omega)$ as the lowest-order description of the metal's response, what is needed are

Fresnel formulas relating electric field amplitudes inside and outside the metal.[22] These naturally separate into two cases, depending on whether the polarization is of the s- or p-wave type. Formally, we will just replace, where necessary, $\mathbf{E}_s \to \mathbf{E}_s^o$, etc., with the superscript o, denoting "outside."

The scattering probability is determined from the ratio of the exiting photon-energy flux to the incident flux. To resolve this with respect to energy loss and scattering angle requires a few manipulations. The energy fluxes follow, via Poynting's theorem, from the absolute squares of field amplitudes.[22] Our present result in (17) is actually a summand, awaiting the sums in (11). When we form the scattered flux outside the metal, we will need, to within factors that are momentarily irrelevant,

$$\Gamma = \left| \frac{1}{T} \sum_{\omega} \frac{1}{A} \sum_{\underset{\sim}{Q}} e^{i(\mathbf{k}_s^o \cdot \mathbf{x} - \omega_s t)} \delta n(-\mathbf{q}, -\omega) \right|^2 , \tag{18}$$

where $\mathbf{k}_s^o = (k_s^o, \underset{\sim}{K}_s)$ with the real-valued

$$k_s^o = \left[\frac{\omega_s^2}{c^2} - K_s^2 \right]^{1/2} = |\mathbf{k}_s^o| \cos\theta_s , \tag{19}$$

and θ_s is the exit angle with respect to the surface normal. To recast Γ into an evaluatable form, first imagine time-averaging it over the period T and space-averaging it over the area A. This process removes the $\mathbf{x}$ and t dependence of Γ, and leaves only single sums on ω and $\underset{\sim}{Q}$. Next imagine that a thermal average of the density fluctuations is done, denoted by $\langle\langle \cdots \rangle\rangle$, so that

$$\langle\langle \Gamma \rangle\rangle = \frac{1}{T^2} \sum_{\omega} \frac{1}{A^2} \sum_{\underset{\sim}{Q}} \langle\langle \delta n(\mathbf{q}^*, \omega) \delta n(-\mathbf{q}, -\omega) \rangle\rangle . \tag{20}$$

We then replace each $\delta n(\mathbf{q},\omega)$ with the equivalent $\int_{-T/2}^{T/2} dt\, e^{i\omega t} \delta n(\mathbf{q},t)$ and use the assertion that the thermal average of a product of density fluctuations only depends on their relative time difference to find

$$\langle\langle \Gamma \rangle\rangle = \frac{1}{T} \sum_{\omega} \frac{1}{A^2} \sum_{\underset{\sim}{Q}} \int_{-T/2}^{T/2} d\tau\, e^{i\omega\tau} \langle\langle \delta n(\mathbf{q}^*, \tau) \delta n(-\mathbf{q}, 0) \rangle\rangle$$
$$\to \int \frac{d\omega}{2\pi} \int \frac{d^2Q}{(2\pi)^2} \left[\frac{1}{A} \int_{-\infty}^{\infty} d\tau\, e^{i\omega\tau} \langle\langle \delta n(\mathbf{q}^*, \tau) \delta n(-\mathbf{q}, 0) \rangle\rangle \right] , \tag{21}$$

where in the second line we have replaced the discrete sums by continuum integrals. With $\langle\langle \Gamma \rangle\rangle$ so written, we can readily resolve the scattering probability into specific energy and momentum transfers.

We now replace

$$\int d^2Q \to \int d^2K_s \to \int |\mathbf{k}_s^o|^2 \cos\theta_s \, d\Omega_s ,$$

where $d\Omega_s$ is a differential element of solid angle describing the exiting photon.[19] To specify it, one needs both θ_s, defined in (19), and ϕ_s, where

$$\cos\phi_s = \hat{K}_i \cdot \hat{K}_s . \tag{22}$$

This definition of ϕ_s as the angle between $\underset{\sim}{K}_i$ and $\underset{\sim}{K}_s$ is consistent with our assumption of isotropy in the surface plane. The remaining angle we need to define is θ_i, the angle of incidence with respect to the surface normal. Now we can write the dimensionless ratio of scattered to incident energy fluxes, I_s/I_i, as

$$\frac{I_s}{I_i} \approx \int d\omega \int d\Omega_s \frac{r_0^2}{\cos\theta_i} \left| \frac{k_s^o}{k_s} \right|^2 \frac{|\mathbf{E}_s^o|^2}{|\mathbf{E}_i^o|^2} V(q,\omega)$$
$$= \int d(\hbar\omega) \int d\Omega_s \, F(\hbar\omega, \Omega_s) . \tag{23}$$

Here, $\mathbf{E}_i^o$ is the amplitude of the incident electric field from outside, which becomes the $\mathbf{E}_i$ of (17) when refracted through the surface, and, similarly, $\mathbf{E}_s^o$ is found from refracting the amplitude $[\hat{\mathbf{k}}_s \times (\hat{\mathbf{k}}_s \times \mathbf{E}_i)]$ of (17) from the metal into vacuum. These vectors are readily found once polarization directions are chosen.

The function V in (23) is given by the density-density correlation function

$$V(\mathbf{q},\omega) = \frac{1}{A} \int_{-\infty}^{\infty} \frac{d\tau}{2\pi} e^{i\omega\tau} \langle\langle \delta n(\mathbf{q}^*, \tau) \delta n(-\mathbf{q}, 0) \rangle\rangle . \tag{24}$$

Using the presumed inversion symmetry in planes parallel to the surface and the absence of a static magnetic field, we can reexpress it as[18]

$$V(\mathbf{q},\omega) = -\frac{\hbar}{\pi} \mathrm{Im} \left[\int_{-\infty}^{0} dx\, e^{-iq^* x} \int_{-\infty}^{0} dx'\, e^{iqx'} \times \chi(x,x';\underset{\sim}{Q},\omega) \right] , \tag{25}$$

where Im denotes "imaginary part of" and χ is the metal's density-response function. The physical definition of χ is that it determines the number density of electrons linearly induced by an applied (external) scalar potential, $\phi_{\mathrm{ext}} = V_{\mathrm{ext}}/e$:

$$\frac{1}{e} \delta\rho_{\mathrm{ind}}(x;\underset{\sim}{Q},\omega) = \int_{-\infty}^{\infty} dx' \chi(x,x';\underset{\sim}{Q},\omega) V_{\mathrm{ext}}(x';\underset{\sim}{Q},\omega) , \tag{26}$$

where $\delta\rho_{\mathrm{ind}}$ is the induced charge density. Specific but approximate χ's will be presented and evaluated in the next section. The relation (25) of V to χ is a particular version of the general fluctuation-dissipation theorem. The dependence of the scattering efficiency, Eq. (23), on V is due to our assumption, Eq. (4), that density fluctuations at plasma frequencies are responsible for the nonlinear response of the metal to the x rays. This nonlinear response, however, has been estimated here by making a first-order correction ($\delta\mathbf{P}$) to a first-order response ($\mathbf{P}$), so

it appears in (23) as a function of linear-response properties alone, i.e., as a function of ϵ_0 at x-ray frequencies and V at plasma frequencies.

To end this section we briefly mention an alternate theoretical approach to the scattering probability which further clarifies the limitations of our approach. One could use a more secure quantum-mechanical method based on time-dependent perturbation theory. To reproduce our answer, it would then be necessary to limit the coupling to

$$H'=\left[\frac{e^2}{2mc^2}\right]\int d^3x\, n(\mathbf{x})\,|\,\mathbf{A}(\mathbf{x})\,|^2\,, \tag{27}$$

where both n and the vector potential $\mathbf{A}$ are treated as operators. Thus the well-known $\mathbf{p}\cdot\mathbf{A}$ coupling has been omitted from our approach, yet, as long as ω_i is far from a core-level threshold, this omission should not be severe.[8,23] It is worth noting that the proper quantum-mechanical treatment has an extra factor of ω_s/ω_i on the right-hand side of (23). Our derivation, as mentioned below (16), cannot discern such factors, which accounts for the $\approx$ sign in (23). It does, however, have the advantage of easily incorporating the important effects of ϵ_0.[19–21]

Finally, we remark that our derivation has presumed a smooth surface. Surface roughness is not necessary for the coupling, but certainly will affect it as well as the dispersion and damping of the surface collective modes. Still we feel that our theory should provide a reasonable first description, since roughness effects should not reduce the coupling strength,[24,25] although they will degrade the energy resolution in regions of significant mode dispersion. Note that our theory does allow for scattering by the surface ripple mechanism,[21,26,27] which occurs if δn contains contributions proportional to $\delta(x)$. The fact that, for x-rays, $\epsilon_0\approx 1$, makes the approximate inclusion of this mechanism less subtle than for visible light.[27,28]

III. MODEL CALCULATIONS

In this section we compute the scattering efficiency—F of (23)—within a model description of the metal's response. The quantity we need is χ of (26), for which we will use results of a recent hydrodynamic derivation.[18] In fact, two distinct χ's came out of that work due to the ambiguity of the choice of additional boundary condition (ABC). The hydrodynamic model does not give a clear indication as to which of the two is better, and a further interest in the present calculation is to quantify how much they differ.

Since the derivation of these χ's is a long process and has already been amply described,[18] we merely quote the results here. For the S case, wherein the ABC imposes zero stress for the electrons at the metal surface,

$$\chi_S(x,x';\underset{\sim}{Q},\omega)=\frac{\omega_p^2}{4\pi e^2\beta^2}\left[-\delta(x-x')+\frac{Q_L^2-Q^2}{2Q_L}(e^{-Q_L|x-x'|}-e^{Q_L(x+x')})\right.$$
$$\left.+\,\delta(x)e^{Q_Lx'}+\delta(x')e^{Q_Lx}+\frac{\beta^2(1-\epsilon)}{\omega_p^2\epsilon}\delta(x)\delta(x')\left[Q_L+Q^2\frac{\epsilon-1}{\epsilon Q_T^o+Q_T}\right]\right]. \tag{28}$$

For the C case, wherein the ABC instead requires zero normal current at the surface,

$$\chi_C(x,x';\underset{\sim}{Q},\omega)=\frac{\omega_p^2}{4\pi e^2\beta^2}\left[-\delta(x-x')+\frac{Q_L^2-Q^2}{2Q_L}[e^{-Q_L|x-x'|}+e^{Q_L(x+x')}(1+\gamma)]\right], \tag{29}$$

with

$$\gamma=2Q^2(1-\epsilon)/[Q_L(\epsilon Q_T^o+Q_T)+(\epsilon-1)Q^2]\,. \tag{30}$$

Both (28) and (29) apply only in $x,x'\le 0$, where the metal is located with constant equilibrium density n_0, spatial dispersion parameter β, and decay rate $1/\tau$. The wavevector components Q_L and Q_T are defined by

$$Q_L^2=Q^2+\frac{\omega_p^2-\omega^2-i\omega/\tau}{\beta^2}\,, \tag{31}$$

$$Q_T^2=Q^2-\frac{\omega^2}{c^2}\epsilon\,, \tag{32}$$

with both Q_L and Q_T chosen to lie in the fourth quadrant. If we replace ϵ in (32) by unity, then $Q_T\to Q_T^o$. The plasma frequency ω_p is given by (3), and

$$\epsilon=1-\frac{\omega_p^2}{\omega^2+i\omega/\tau}\,. \tag{33}$$

We remark that here ω_p and ϵ refer to the response of the mobile electrons at plasma frequencies. In contrast, the ϵ_0 (ω_i or ω_s) that implicitly enters (23) describes the system's linear response at x-ray frequencies, and should be determined from experimental data, and not (2), which only motivated the ansatz (4).

We now rewrite the F of (23) as

$$F=\left[\frac{r_0^2\omega_p}{4\pi^2e^2c}\right]\left[\left|\frac{k_s^o}{k_s}\right|^2\frac{|\,\mathbf{E}_s^o\,|^2}{|\,\mathbf{E}_i^o\,|^2}\frac{1}{\cos\theta_i}\right]$$
$$\times\left[\frac{4\pi^2e^2c}{\hbar\omega_p}V(\mathbf{q},\omega)\right] \tag{34a}$$

$$=\left[\frac{r_0^2\omega_p}{4\pi^2e^2c}\right]F_KF_D\,. \tag{34b}$$

The first factor in (34a) carries the units of F,

$$\frac{r_0^2\omega_p}{4\pi^2e^2c}=1.06\times10^{-14}/\text{eV}\ \ [\hbar\omega_p/(15\text{ eV})]\ , \tag{35}$$

while the second factor, called F_K in (34b), is kinematic since it depends only on the scattering configuration and properties at the x-ray frequencies. In our calculations, we set $\hbar\omega_p=15$ eV, $\omega_i=\omega_s=100\omega_p$, and $\epsilon_0-1=-10^{-4}+i10^{-5}$ at both ω_i and ω_s. The critical angle of incidence θ_c is then approximately $\pi/2-0.01$, and we choose $\theta_i=89.5°$, which is just beyond θ_c. This choice considerably reduces the penetration depth of the incident x ray into the metal and gives a large value for $(\cos\theta_i)^{-1}$ in F_K. However, this last advantage is lost upon further increases in θ_i, since $\mathbf{E}_i$ of (9) eventually goes to zero as $\cos\theta_i$ for any polarization. We have done calculations assuming either s or p-wave incident polarizations and summing over all final polarizations. The factor F_K depends very slightly on ϕ_s or incident polarization over the angle ranges that we consider.

The third factor in (34a), called F_D in (34b), depends on the electrons' dynamics near the plasma frequency. Like F_K, it is dimensionless and may be analytically expressed by combining (34a) and (25) with either (28) or (29). The latter two formulas explicitly, but distinctly, account for the possible effect of the metal's surface on collective modes of density oscillation. They should be contrasted to the hydrodynamic result for χ in a homogeneous bulk metal,

$$\chi^{(B)}(x,x';\underset{\sim}{Q},\omega)=\frac{\omega_p^2}{4\pi e^2\beta^3}\left[-\delta(x-x')+\frac{Q_L^2-Q^2}{2Q_L}e^{-Q_L|x-x'|}\right], \tag{36}$$

which implies, when integrated over $x,x'\le0$,

$$F_D^{(B)}=\frac{\omega_p c}{\beta^2}\text{Im}\left[\frac{Q_L^2-Q^2}{Q_L^2+q^2}\left[\frac{1}{2\,\text{Im}q}\right]+\frac{(Q_L^2-Q^2)/2Q_L}{(Q_L-iq)(Q_L-iq^*)}\right]. \tag{37}$$

If we call $L=(-2\,\text{Im}q)^{-1}$ the effective depth of the metal seen by the x rays, and formally imagine $L\to\infty$, then

$$F_D^{(B)}\to\frac{Lc}{\omega_p}(Q^2+q^2)\text{Im}\left[\frac{-1}{\epsilon^{(B)}(\mathbf{q},\omega)}\right], \tag{38}$$

where

$$\epsilon^{(B)}(\mathbf{q},\omega)=1-\omega_p^2/(\omega^2+i\omega/\tau-\beta^2|\mathbf{q}|^2)\ . \tag{39}$$

Equation (38) shows the well-known dependence for inelastic light scattering from density fluctuations in bulk metal.[23,29,30] Within the hydrodynamic model, only bulk plasmons contribute to the loss spectrum; particle-hole excitations are not allowed. Still, by using a large scattering rate, $\omega_p\tau=10$, we can partially mimic their effect.[31,32] We also satisfactorily represent the bulk-plasmon dispersion by choosing $\beta=0.01c$. As discussed in the Introduction, bulk-plasmon losses have already been observed,[7,8]

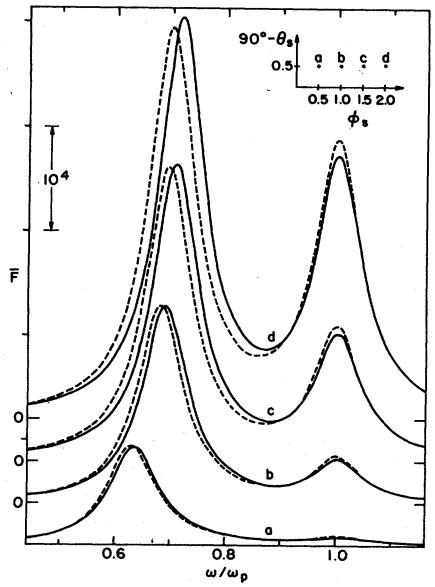

FIG. 1. Scattering efficiency parameter $\bar{F}$ vs x-ray frequency loss ω for s-polarized x rays incident at $\theta_i=89.5°$. The inset shows (in deg) the scattering angles used. See text for other parameter choices. The dashed curves employ the χ_s of (28), the solid curves the χ_c of (29). Each pair of curves has been offset vertically for clarity.

and our focus is instead on the modification of this scattering due to the surface. In order to enhance the relative size of these changes, we must reduce L in (38). It is for this reason that we work with grazing angles of incidence and exit. When either θ_i or θ_s goes beyond θ_c, L is reduced by about 2 orders of magnitude for our choice of ϵ_0.

In Figs. 1–3 we show typical results for

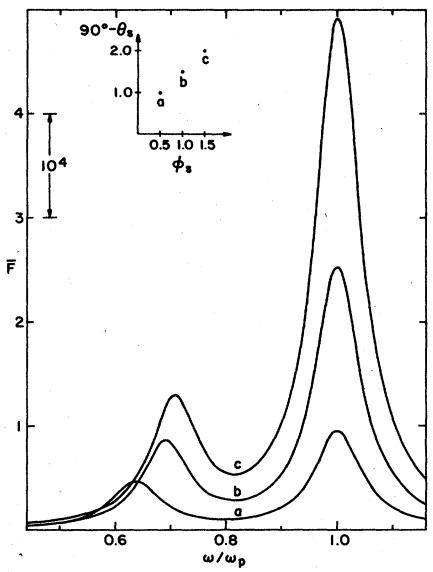

FIG. 2. Scattering efficiency parameter $\bar{F}$ vs x-ray frequency loss ω for s-polarized x rays incident at 89.5°. The labeling scheme is the same as in Fig. 1, except that only the C case of (29) is shown and no offset made.

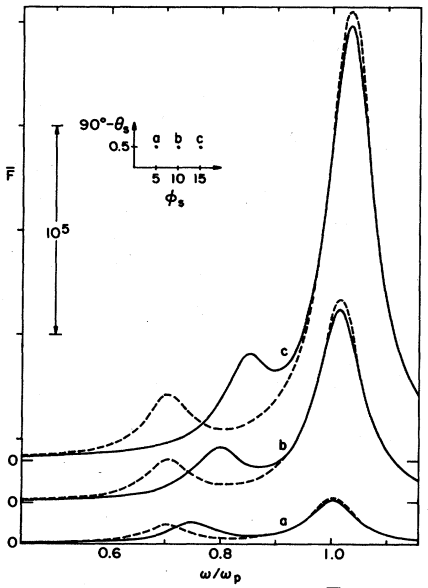

FIG. 3. Scattering efficiency parameter $\bar{F}$ vs x-ray frequency loss ω for s-polarized x rays incident at $\theta_i=89.5°$. The labeling scheme is the same as in Fig. 1.

$$\bar{F}=F_K F_D \ , \tag{40}$$

the product of the kinematic and dynamic factors in (34b). Surface-plasmon losses are apparent in each figure, but their relative importance quickly decreases as the scattering angles move away from the specular direction $\theta_s=\theta_i$, $\phi_s=0°$. As a very rough estimate, we found that in F_D the surface-plasmon peak height scales as Q, while that for the bulk plasmon scales as $(Q^2+q^2)L$. These imply that, in moving away from the specular direction, it is preferable to increase $|\phi_s|$ rather than $|\theta_s-\theta_i|$. This qualitative rule is supported by a comparison of Figs. 1 and 2. We also computed spectra in which θ_s was varied with fixed $\phi_s=0°$. The surface-plasmon peak suffered, relatively, even more than in Fig. 2 as one went away from the specular direction.

The magnitudes of $\bar{F}$ should be carefully noted since they, in combination with (35), determine the experimental feasibility of observing such spectra. Results for incident p waves differ by less than 1% for angles scanned in Figs. 1–3. The kinematic factor lies between 300 and 750, and is mostly due to $(\cos\theta_i)^{-1}=115$. The remainder results from being close to θ_c. There is essentially no dependence of F_K on ω. The dynamic factor is responsible for the loss peaks. It can be further increased by increasing Q, but the relative size of the surface-plasmon loss then decreases. Thus it seems that at resolvable surface-loss peaks, F is a few times 10^{-10}/eV. One would need then an incident flux of 10^{12} photons/sec eV striking the surface in order to produce (ideally) one scattered-photon/eV sec within a solid angle spanned by $\Delta\phi_s\approx 10°$, $\Delta\theta_s\approx 1°$. These estimates are admittedly crude, but should give the correct order of magnitude. Such an incident flux at x-ray frequencies is close to present capabilities.[15–17]

The above estimates do not depend on hydrodynamic ABC's. Both the S and C cases yield a coupling to x rays that is basically the same, even though the spatial distribution of their charge-density fluctuations are quite different; see Eqs. (28) and (29). The reason for this is that the magnitude of q is small compared to Q_L, so whether a charge fluctuation is proportional to $\delta(x)$ or to $\theta(-x)Q_L e^{Q_L x}$ is immaterial.

Where the two models do show a difference is in the dispersion of the surface-plasmon frequency. This dispersion arises from the effect of the two speeds present in the problem.[33] At low Q, c has the dominant influence, forcing

$$\omega(Q)\underset{Q\to 0}{\to} cQ \ , \tag{41}$$

where $\omega(Q)$ is the surface-plasmon frequency, formally defined by the location of the pole in χ when $1/\tau=0$. For the S case it results from the vanishing of $\epsilon Q_T^0+Q_T$, while for the C case it requires $Q_L(\epsilon Q_T^0+Q_T)=(1-\epsilon)Q^2$. The limit (41) is, for both cases, the sole nonradiative (i.e., $\omega<cQ$) solution of these requirements. As Q increases through ω_p/c, (41) gives way to a (nonretarded) behavior that depends on ABC's, and possibly on the other speed, β. For the S case, $\omega(Q)$ saturates at $\omega_p/\sqrt{2}$, while for the C case it continues to increase, eventually merging into the bulk-plasmon band, whose bottom edge is given by $\omega^2=\omega_p^2+\beta^2Q^2$. These qualitative differences become especially evident in Fig. 3, where the Q's are sufficiently large that even the bulk plasmon begins to show some dispersion. The ability of inelastic x-ray scattering to discriminate between the two cases is one of its attractions. One also could follow the width of the loss peaks as a function of $\mathbf{q}$ in order to deduce the correct lifetime of the collective modes and the influence of single-particle excitations. Such data would complement those found by electron-loss experiments.[3,4,31] It is worth noting in this regard that the coupling for electron scattering decreases with increasing momentum transfer, while that for x-ray scattering grows.

In summary, let us stress that our primary motivation in this paper has been to stimulate experimental interest. The theoretical estimates are not the most sophisticated possible, but should serve as useful guides. The calculations are straightforward and could be readily adapted to alternate experimental configurations and tailored to specific material applications. However, a more fundamental need is for some experimental data in order to confirm the basic ideas outlined here, and to suggest how they should be refined. Such studies will reveal most clearly the potential utility of inelastic x-ray scattering from surface plasmons.

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