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Influence of the electron density profile on surface plasmons in a hydrodynamic model[*]

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The effect of the electron density profile at the surface of a metal on the surface-plasma modes is studied within the framework of a hydrodynamic model. For a sufficiently diffuse surface, higher multipole excitations can exist in addition to the usual surface plasmon. The frequency of both kinds of modes is studied in the long-wavelength limit.

Recently several authors[1,2] have investigated the sensitivity of surface plasmons to the electron density profile at the surface. Feibelman[1] has shown that in the random-phase approximation (RPA) the frequency of a surface plasmon of infinite wavelength is independent of the density profile, but that at shorter wavelengths both the dispersion and damping are affected. Bennett[2] has studied how the electron density distribution affects the surface-plasmon dispersion by numerically solving the equations of a simple hydrodynamic model with a density profile which decreases linearly through a surface region from the bulk value to zero. In addition to its effect on the dispersion relation, Bennett found that for a sufficiently diffuse surface additional modes could occur. The numerical nature of Bennett's results makes it difficult to obtain insight into the physical origin of the additional modes and why they do not appear in the work of Feibelman and of Beck and Celli. The object of the present paper is to present a hydrodynamic model based on a quasistatic generalization of the density-functional formalism[3] and to obtain approximate analytical results which clarify the connection between the results of Bennett and those obtained in the RPA. In addition we wish to emphasize that the higher surface modes discussed here could be a very useful tool in the experimental study of the surface electron density, especially of chemisorbed species on metallic surfaces.

The basic equations in this hydrodynamic model are the equation of continuity, Euler's equation, and Poisson's equation:

$$\frac{\partial}{\partial t} n + \vec{\nabla}\cdot n\vec{v} = 0, \tag{1}$$

$$n\left(\frac{\partial}{\partial t}\vec{v} + (\vec{v}\cdot\vec{\nabla})\vec{v}\right) = -n\vec{E} - n\vec{\nabla}\left(\frac{\delta G}{\delta n}\right), \tag{2}$$

$$\vec{\nabla}\cdot\vec{E} = 4\pi(N_+ - n + \rho_0). \tag{3}$$

In these equations $n(\vec{r}, t)$ is the electron density, $N_+(z)$ is the positive background density, and $\rho_0(\vec{r}, t)$ is the density of some external perturbation. (Unless otherwise stated we use atomic units, $m = |e| = \hbar = 1$ in this paper.) The hydrodynamic velocity is given by $\vec{v}(\vec{r}, t)$, and the self-consistent electric field by $\vec{E}(\vec{r}, t)$. In Euler's equation there occurs the universal energy functional $G\{n(\vec{r}, t)\}$ which includes the kinetic, exchange, and correlation energies of the inhomogeneous electron system. Note that the quantity $n\vec{\nabla}(\delta G/\delta n)$ plays the role of the gradient of the pressure in classical fluids. Implicit in Eq. (2) is an adiabatic extension of the ground-state density-functional formalism.[4]

In order to describe small-amplitude self-sustaining oscillations, we assume that in the absence of any ρ_0 there exists a small deviation from thermal equilibrium of the form $f(\vec{r}, t) = f(z)e^{iqy-i\omega t}$, where q is the wave vector in the plane of the surface, and we linearize Eqs. (1)–(3). The density and self-consistent scalar potential ($\vec{E} = -\vec{\nabla}\phi$) are written as $n(\vec{r}, t) = n_0(z) + n_1(\vec{r}, t)$ and $\phi(\vec{r}, t) = \phi_0(z) + \phi_1(\vec{r}, t)$. We emphasize that though $\phi_0(z)$ does not appear explicitly in Eq. (5) below, it is effectively taken into account via the self-consistent density $n_0(z)$. The linearized hydrodynamic equations can then be combined to give the equation

$$\omega^2 n_1 = \vec{\nabla}\cdot(n_0\vec{\nabla}\phi_1) - \vec{\nabla}\cdot[n_0\vec{\nabla}(\delta G/\delta n)_1], \tag{4}$$

where

$$\left(\frac{\delta G}{\delta n}\right)_1 \equiv \int d^3r' \left(\frac{\delta^2 G\{n\}}{\delta n(\vec{r})\delta n(\vec{r}\,')}\right)_{n_0} n_1(\vec{r}\,', \omega).$$

Casting this equation in operator notation by writing $(\delta G/\delta n)_1 = \hat{\mathfrak{L}}\{n_0\}n_1$, we can write Eq. (4) in the form

$$\omega^2 n_1(z) = \frac{\partial}{\partial z}\left(n_0(z)\frac{\partial}{\partial z}\phi_1(z)\right) - q^2 n_0(z)\phi_1(z) - \frac{\partial}{\partial z}\left(n_0(z)\frac{\partial}{\partial z}\hat{\mathfrak{L}}\{n_0\}n_1\right) + q^2 n_0(z)\hat{\mathfrak{L}}\{n_0\}n_1. \tag{5}$$

The potential ϕ_1 is related to the density n_1 by the equation

$$\phi_1(z, q\omega) = \frac{-2\pi}{q}\int dz'\, e^{-q|z-z'|} n_1(z', q, \omega). \tag{6}$$

In Eq. (6) we include explicitly the dependence of ϕ_1 and n_1 on q and ω for emphasis. This dependence is implicit in Eq. (5) and in the remainder of the paper. We substitute Eq. (6) into Eq. (5) and integrate with respect to z, making the assumption that the density fluctuation n_1 associated with the surface excitation is sufficiently well localized that there exists a finite length L such that for $|z| > L$, both $n_1(z)$ and $\hat{\mathfrak{L}} n_1$ vanish. Note that although the operator $\hat{\mathfrak{L}}$ does not appear explicitly in the integrated equation, many-body effects associated with it are implicitly contained through $n_1(z)$ which must be a solution of Eq. (5). For wavelengths sufficiently long that $qL \ll 1$ we expand in powers of q and obtain

$$\omega^2 = \omega_{\mathrm{sp}}^2 - \tfrac{1}{2} q \left\langle z \frac{\partial}{\partial z} \omega_p^2(z) \right\rangle + \tfrac{1}{2} q [\omega_p^2(L) - \omega_p^2(-L)] \times \langle n_1(z) \rangle^{-1} \langle z n_1(z) \rangle + O(q^2) \ , \tag{7}$$

where the symbol $\langle f(z) \rangle$ stands for $\int_{-L}^{L} dz\, f(z)$. Here $\omega_p^2(z) = 4\pi n_0(z)$, $\omega_p^2(\pm L)$ is the value of $\omega_p^2(z)$ at $z = \pm L$, and ω_{sp}, the "regular" surface-plasmon frequency, is given by $\omega_{\mathrm{sp}}^2 = \frac{1}{2}[\omega_p^2(L) + \omega_p^2(-L)]$. The differential equation for $n_1(z)$ has coefficients which are analytic functions of q; therefore we expect $n_1(z)$ to be analytic in q and expandable in power series,

$$n_1(z) = \sum_{l=0}^{\infty} f_l(z) q^l \ . \tag{8}$$

By substituting Eq. (8) in Eq. (6) we see immediately that in order for $\phi_1(z)$ to be finite when q approaches zero, it is necessary that $\int f_0(z)\, dz = 0$. Now, if[5] $f_0(z) \equiv 0$, Eq. (7) becomes formally the RPA result for the "regular" surface plasmon or monopole charge fluctuation obtained by Harris and Griffin,[2] namely,

$$\omega^2 = \omega_{\mathrm{sp}}^2 + \tfrac{1}{2} q [\omega_p^2(L) - \omega_p^2(-L)] \langle f_1(z) \rangle^{-1} \langle z f_1(z) \rangle - \tfrac{1}{2} q \left\langle z \frac{\partial}{\partial z} \omega_p^2(z) \right\rangle + O(q^2), \tag{9}$$

where, from Eqs. (5), (6), and (8), $f_1(z)$ satisfies the equation

$$\frac{\partial}{\partial z}\left(n_0(z) \frac{\partial}{\partial z} (\hat{\mathfrak{L}} f_1) \right) + \omega_{\mathrm{sp}}^2 f_1(z) - \frac{1}{2} \frac{\partial}{\partial z}\left(\omega_p^2(z) \int_{-L}^{L} dz'\, \mathrm{sgn}(z - z') f_1(z') \right) = 0. \tag{10}$$

Only the $q = 0$ limit of $\hat{\mathfrak{L}}$ enters in this equation. We emphasize that Eq. (9) is a general result, valid no matter what (self-consistent) electron density profile is used and for all dynamical models for the energy functional (as long as the resulting $\hat{\mathfrak{L}}$ is sufficiently short ranged). As in the RPA result, the infinite wavelength limit $\omega^2 = \omega_{\mathrm{sp}}^2$ is independent of the electron density profile, but the coefficient of the term linear in q depends on the numerical value of $\langle f_1 \rangle^{-1} \langle z f_1 \rangle$ which, being a functional of $n_0(z)$, is expected to depend on this profile. If $f_0(z) \neq 0$, Eq. (7) becomes

$$\omega^2 = \omega_{\mathrm{sp}}^2 + \tfrac{1}{2}[\omega_p^2(L) - \omega_p^2(-L)] \langle f_1(z) \rangle^{-1} \times \langle z f_0(z) \rangle + O(q) \ , \tag{11}$$

where $f_0(z)$ and $f_1(z)$ satisfy the equations

$$\frac{\partial}{\partial z}\left(n_0(z) \frac{\partial}{\partial z} (\hat{\mathfrak{L}} f_0) \right) + \omega^2 f_0(z) - \frac{1}{2} \frac{\partial}{\partial z}\left(\omega_p^2(z) \times \int_{-L}^{L} dz'\, \mathrm{sgn}(z - z') f_0(z') \right) = 0, \tag{12}$$

and

$$\frac{\partial}{\partial z}\left(n_0(z) \frac{\partial}{\partial z} (\hat{\mathfrak{L}} f_1) \right) + \omega^2 f_1(z) - \frac{1}{2} \frac{\partial}{\partial z}\left(\omega_p^2(z) \times \int_{-L}^{L} dz'\, \mathrm{sgn}(z - z') f_1(z') \right) = \frac{1}{2} \left(\frac{\partial}{\partial z} \omega_p^2(z) \right) \langle z f_0(z) \rangle. \tag{13}$$

The first two terms on the right-hand side of Eq. (11) give the square of the frequency of a higher "multipole" charge fluctuation of infinite wavelength. The condition $\int dz\, f_0(z) = 0$ leads to the rather satisfying intuitive classification of dipole, quadrupole, etc., charge fluctuation[6] for these modes, as distinguished from the "regular" surface plasmon ("monopole" fluctuation) for which the leading term, f_1, in the expansion of $n_1(z)$ has a nonzero integral. Note that the $q = 0$ limit of the frequency of the higher multipoles depends quite sensitively on the electron density profile, as is obvious from the equations satisfied by $f_0(z)$ and $f_1(z)$.

In order to illustrate the physical concepts involved in the above discussion we first present solutions for an extremely simple model, similar to that employed by Bennett,[2] which consists of assuming the pressure term to have the simple form[7]

$$n_0 \vec{\nabla} (\delta G / \delta n)_1 = \beta^2 \vec{\nabla} n_1, \tag{14}$$

where β^2 is a constant.

In addition, in order to describe a metal-vacuum interface, we assume that $n_0(z)$ vanishes at some point on the z axis which we choose as the origin. With this approximation, and defining

$$g(z) \equiv \frac{1}{2} \int_{-\infty}^{0} dz'\, \mathrm{sgn}(z - z') f_1(z'),$$

Eq. (10) becomes (note that $\partial g / \partial z = f_1$)

$$\frac{\partial^2 g(z)}{\partial z^2} + \frac{1}{\beta^2} [\omega_{\mathrm{sp}}^2 - \omega_p^2(z)] g(z) = \frac{\omega_{\mathrm{sp}}^2}{2\beta^2} \int_{-\infty}^{0} dz'\, f_1(z') = \frac{\omega_{\mathrm{sp}}^2}{\beta^2} g(0^-). \tag{15}$$

Now, $f_1(z)$ is subject to the boundary condition that it vanish at $z = -\infty$ (deep inside the metal) and for all $z > 0$. This condition on $f_1(z)$ automatically insures the vanishing of the normal component of the current density at the origin, so no additional boundary condition on the current is needed. This result, which can be verified by evaluating Eq. (15) at $z = 0^-$, is a consequence of our having chosen $\omega = \omega_{sp}$ in Eq. (10) as is required by Eq. (9). For the higher multipole fluctuations Eq. (12) can be expressed as

$$\frac{\partial^2 h(z)}{\partial z^2} + \frac{1}{\beta^2}\,[\omega^2 - \omega_p^2(z)]h(z) = 0, \tag{16}$$

where

$$h(z) \equiv \frac{1}{2}\int_{-\infty}^{0} dz'\, \mathrm{sgn}(z - z') f_0(z') \qquad \left(\frac{\partial h(z)}{\partial z} \equiv f_0(z)\right),$$

together with the boundary condition $h(z = 0^-) = 0$ [which is equivalent to $\int_{-\infty}^{0} dz\, f_0(z) = 0$]. Equation (16) is of the form of a simple one-dimensional Schrödinger equation, so the existence of higher multipole modes has been reduced to finding the eigenstates of a one-dimensional potential. By evaluating Eq. (16) at $z = 0^-$ one can demonstrate that the condition $\int_{-\infty}^{0} dz\, f_0(z) = 0$ guarantees conservation of charge, so again no additional boundary condition is needed. We emphasize that the eigenvalues ω^2 obtained from solving Eq. (16) are consistent with the general expression, Eq. (11), into which solutions f_0 and f_1 of Eqs. (12) and (13) have been substituted, only if charge is conserved.

An instructive example which is exactly soluble[8] is that of a "potential function" $\omega_p^2(z) = \omega_p^2(1 - \cosh^{-2}\alpha z)$ where ω_p is the plasma frequency deep inside the metal. The parameter α characterizes the diffuseness of the surface. The solid is in the region $z < 0$.

First we solve the (inhomogeneous) equation for the regular surface plasmon, Eq. (15). For simplicity we chose the product $\alpha\beta$ to equal $\omega_p/\sqrt{2}$ in which case the two solutions to the homogeneous equation can be expressed in terms of hyperbolic functions. We show below that this value of $\alpha\beta$ corresponds to a surface diffuseness such that, in this model, the dipole mode first appears. If, following Bennett we take $\beta^2 = \frac{3}{5}v_F^2$ and use data for sodium (the resulting profile is shown as curve "a" in Fig. 1), we obtain from Eq. (9) $\omega^2 = \frac{1}{2}\omega_p^2(1 - 0.08q)$, with q in Å^{-1}. It is a straightforward exercise to show that for a step-function density profile one obtains $\omega^2 = \frac{1}{2}\omega_p^2(1 + 1.37q)$ and this indicates that (as first shown by Bennett) the slope of regular plasmon dispersion changes sign as the diffuseness of the electron contour increases from zero.[9] Furthermore, the result implies that this change in sign occurs when the diffuseness is close to that which first binds the dipole mode.

The zero-point energy of the higher multiple modes for this potential function was found by solving Eq. (16) with the boundary condition $h(z = 0) = 0$. This restricts us to the odd-parity solutions whose eigenfrequencies are given by

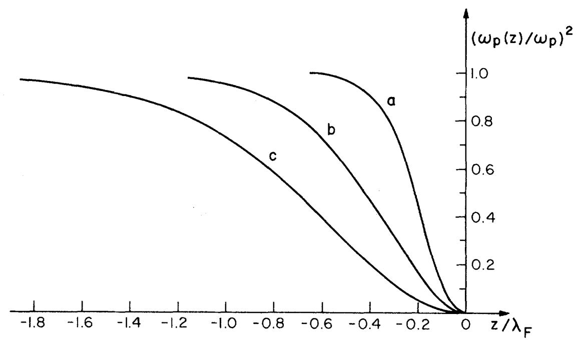

FIG. 1. Electron density profiles $n_0(z)/n_0(-\infty) = \omega_p^2(z)/\omega_p^2 = 1 - \cosh^{-2}\alpha z$ for three different values of α. Curves a, b, and c correspond to α equal to 0.73 Å^{-1}, 0.29 Å^{-1}, and 0.18 Å^{-1}, respectively. Abscissa is measured in Fermi wavelengths ($\lambda_F = 2\pi/k_F$) appropriate to sodium (one Fermi wavelength equals 6.28 Å).

$$\omega_n^2 = \omega_p^2 - (\alpha\beta/2)^2[-1 - 2n + (1 + 4\omega_p^2/\alpha^2\beta^2)^{1/2}]^2,$$

where n takes on the values 1, 3, 5, ... subject to the condition $2n < -1 + (1 + 4\omega_p^2/\alpha^2\beta^2)^{1/2}$. We give here the values of $\alpha\beta$ at which successively higher multipole fluctuations first appear and the corresponding zero-point energies. For $\alpha\beta = \omega_p/\sqrt{2}$ the dipole fluctuation first appears, with frequency $\omega = \omega_p$. For $\alpha\beta = \omega_p/\sqrt{12}$ the quadrupole fluctuation appears at $\omega = \omega_p$, and the dipole fluctuation has a frequency $\omega = (\frac{2}{3})^{1/2}\omega_p$. For $\alpha\beta = \omega_p/(30)^{1/2}$ the octopole mode has $\omega = \omega_p$, while the dipole occurs at $\omega = (\frac{7}{15})^{1/2}\omega_p$, which is less than the regular surface-plasmon frequency, and the quadrupole at $\omega = (\frac{23}{30})^{1/2}\omega_p$. The curves a, b and c of Fig. 1 are the profiles corresponding to these values of $\alpha\beta$ (for the bulk density of sodium).

Our qualitative results based on the simple profiles just described lead us to suggest the usefulness of performing inelastic low-energy electron diffraction experiments on layers of alkalies chemisorbed on free-electron metal surfaces. By appealing to the simple model of chemisorption proposed by Lang[10] to explain changes in work function as a function of coverage, we would expect that the higher multipole fluctuations described in this paper (which do not appear to have been detected in experiments performed on clean surfaces) could be observed when the coverage is high enough (perhaps one or two full layers). The simple *Ansatz* made in Eq. (14) and the model profiles discussed above illustrate the basic concepts in a qualitative way. However, the hydrodynamic model proposed in this paper is more generally valid than these simple assumptions. In order to obtain quantitative answers a more rigorous choice for the density functional and a self-consistent density profile

$n_0(z)$ must be used. Lang and Kohn[11] and Lang[10] determined numerically the self-consistent density profile $n_0(z)$ for clean surfaces and for surfaces with chemisorbed species, and we expect to use their numerical results. An approximate energy functional which has been useful in static studies of metallic surfaces is the first-gradient expansion.[3,12] Since the gradient of the density appears in this approximate functional $G\{n(\vec{r}, t)\}$, the operator $\hat{\mathfrak{L}}$ appearing in Eq. (5) becomes a second-order differential operator, and the equations satisfied by f_0 and f_1 become fourth-order equations. With these complications it will be necessary to resort to numerical methods to obtain quantitative results, but we expect the qualitative features of the simpler models to remain.

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[5] With $f_0(z) = 0$, Eq. (6) shows that the zeroth-order term in the fluctuating potential is a constant (independent of z) which corresponds to Feibelman's *Ansatz* for the $q = 0$ behavior of the RPA potential associated with the "regular" surface plasmon. Note that for the other branches of the dispersion relation, i.e., for $f_0(z) \neq 0$, $\int dz f_0(z) = 0$, the zeroth-order potential does depend on z.

[6] Similar results for a series of higher modes of a nonuniform plasma slab were obtained for a classical plasma by F. C. Hoh, Phys. Rev. 133, A1016 (1964).

[7] While this choice is not identical to that of Bennett, it is linear in n_1 and leads to the correct bulk-plasmon dispersion if Bennett's choice $\beta^2 = \frac{3}{5} v_F^2$ is made.

[8] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Addison-Wesley, Reading, Mass., 1965).

[9] In order to check this conclusion we solved Eq. (15) for a different potential function, $\omega_p^2(z) = \omega_p^2(1 - e^{2\lambda z})$ which is also amenable to analytical solution [see, for example, P. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill, New York, 1953)]. For simplicity we chose $\lambda = \sqrt{2}\, \omega_p/\beta$ in which case the solutions to the homogeneous equation are $J_{\pm 1/2}(e^{\lambda z}/\sqrt{2})$. We obtained $\omega^2 = \frac{1}{2} \omega_p^2(1 + 1.32q)$ (q in Å^{-1}). The corresponding profile (which is not diffuse enough to bind higher modes) is closer to the step-function profile than the smooth profile discussed in the text.

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