Hydrodynamic description of surface plasmons: Nonexistence of the unrestricted half-space solution

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The surface plasmon solution of the hydrodynamic model is reinvestigated. It is demonstrated that the extreme sensitivity of the dispersion on the approximation of the surface profile is intimately related to the nonexistence of the half-space solution if the vacuum region extends to infinity. A remedy of this flaw is proposed. [S0163-1829(99)08447-7]

I. INTRODUCTION

Since the pioneering work of Ritchie[1] collective electronic excitations at the boundary of metallic systems are of continuous interest in solid state research. In particular, the identification of the relevant parameters that govern the dispersion and damping of surface plasmons have been an important topic and considerable progress has been achieved, e.g., Refs. 2–5. For example, the frequency $\omega_{sp}(q)$ of the surface plasmons at small wave vectors q becomes independent of the surface charge profile but the slope of the dispersion $(=c_s)$ is affected. For a plane surface and neglecting retardation we have

$$\omega_{sp}(q)=\frac{\omega_p}{\sqrt{2}}+c_s q+O(q^2), \quad q\ll k_F. \tag{1}$$

Here, $\omega_p=(n_0e^2/m\epsilon_0)^{1/2}$ is the bulk plasma frequency, $k_F=(3\pi^2 n)^{1/3}$ is the Fermi-wave vector, n_0 is the bulk electron density, m is the electron mass, and e is the elementary charge.

Most of the dynamical calculations can be divided into two categories: model calculations [macroscopic electrodynamics in terms of bulk dielectric functions, hydrodynamic (HD) descriptions] and quantum theories (random phase approximation, time-dependent density functional theory). The latter are of formidable mathematical and numerical complexity so that the HD description until today serves as a useful model for the description of collective electronic excitations, e.g., Refs. 6–20.

The HD description is based on a set of partial differential equations for the particle– and velocity densities $n(\mathbf{r},t)$, $\mathbf{v}(\mathbf{r},t)$ of the charge carriers. Within this model theoretical studies of surface plasmons have been almost exclusively performed in connection with ''rigid'' boundary conditions, i.e., vanishing of the normal component of $\mathbf{v}(\mathbf{r},t)$ at the geometrical boundary of the fixed positive charge background or outside a finite distance from the geometrical surface. The latter condition yields a tractable model and has a distinguished history, e.g. Ref. 9. It also offers the possibility to ''smuggle in'' the spill-out of the electron density across the geometrical surface which is of quantum origin.[21]

All too often is heard the alibi that since the theory itself is only approximate, the mathematics needs to be no better. In truth the opposite follows (as stated by Barton[9]). The aim of this paper is to draw attention to a rather unpleasant flaw of the HD model which – to our knowledge – has been overlooked before: The solution of the hydrodynamic equations ceases to exist when extending the vacuum region to infinity. This property is intimately connected with the occurance of multipole surface excitations if the (steady state) electronic surface profile extends considerably across the geometrical boundary of the metal surface and becomes stronger the more the profile cut off is shifted to infinity. This is puzzling as the existence of multipole surface excitations have been demonstrated both experimentally and theoretically, e.g., Refs. 4,5,12,22 and 23. Ahlqvist and Apell,[11] however, concluded that these modes are artificial within the HD model depending on the choice of the surface profile.

For a discussion and overview of surface effects in the HD model we refer to the article by Barton.[9] A general overview on plasmons in the bulk and at the surface of metallic systems and clusters may be found, e.g., in Ref. 24. The HD model is a time–dependent generalization of the Thomas–Fermi model, which is successfully used for the semiclassical description of atoms.[25]

Our paper is organized as follows: Sec. II summarizes the basic equations in dimensionless form and gives the relevant steady state solution. Sec. III provides the linearized equations which are discussed in Section IV for finite as well as unrestricted surface regions. Section V contains our conclusions and a proposed remedy of the flaw.

II. BASIC EQUATIONS

The basic equations of the HD description are the continuity and Euler equations that govern the particle density $n(\mathbf{r},t)$ and velocity density $\mathbf{v}(\mathbf{r},t)$ of the (mobile) electrons and the Maxwell equations.

$$N(\mathbf{r},t)\frac{\partial \mathbf{V}(\mathbf{r},t)}{\partial t}=-N(\mathbf{r},t)\mathbf{E}(\mathbf{r},t)-\mathrm{grad}P(\mathbf{r},t), \tag{2}$$

$$\frac{\partial N(\mathbf{r},t)}{\partial t}=-\mathrm{div}\,[N(\mathbf{r},t)\mathbf{V}(\mathbf{r},t)], \tag{3}$$

$$\mathrm{div}\mathbf{E}(\mathbf{r},t)=N_+(\mathbf{r})-N(\mathbf{r},t)+N_{ext}(\mathbf{r},t), \tag{4}$$

$$\mathrm{curl}\,\mathbf{E}(\mathbf{r},t)=0, \tag{5}$$

where

$$P(\mathbf{r},t)=CN^{\alpha}(\mathbf{r},t). \tag{6}$$

$N_{+}(\mathbf{r})$ denotes the charge density of the rigid positive background and $N_{ext}(\mathbf{r},t)$ is an external electron distribution, if present, e.g., in an electron–energy–loss experiment. For notational simplification we have used dimensionless quantities with

$$r\leftarrow\frac{\omega_p}{v_F}r,\quad t\leftarrow\omega_p t,\quad q\leftarrow\frac{v_F}{\omega_p}q,$$

$$N\leftarrow n/n_0,\quad \mathbf{V}\leftarrow\mathbf{v}/v_F,\quad \mathbf{E}\leftarrow\mathbf{E}/E_0,\quad P\leftarrow P/P_0,$$

where $v_F=\hbar k_F/m$ is the Fermi-velocity and $E_0=\hbar\omega_p k_F/e$, $P_0=mv_F^2 n_0$, respectively denote characteristic amplitudes for the (total) electric field $\mathbf{E}(\mathbf{r},t)$ and (adiabatic) pressure $P(\mathbf{r},t)=P[N(\mathbf{r},t)]$. The term $\mathbf{v}\,\mathrm{grad}\,\mathbf{v}$ has been omitted in Eq. (2) as we are solely interested in linear excitations. Furthermore, we ignored retardation and magnetic effects, as these are only relevant at very small wave vectors $q<\omega_p/c(\approx 10^{-2}\ \text{Å}^{-1}$ for Al).

For the degenerate, noninteracting electron gas $C=1/5$, $\alpha=5/3$, whereas the correct high-density limit [=random phase approximation] of the plasmon dispersion requires $C\alpha=3/5$. There has been some attempts to include exchange and correlation effects in the pressure functional.[26] For our purpose, however, it is sufficient to approximate $P(\mathbf{r},t)$ by a power law $P=CN^{\alpha}$ and adjust C, α so that the correct (experimental or theoretical) bulk plasmon dispersion is reproduced at small wave vectors

$$\omega_{bp}(q)=\omega_p+c_b q^2+O(q^4),\quad c_b=C\alpha/2. \tag{7}$$

For a plane, rigid ionic charge profile we have $N_{+}(\mathbf{r})=\theta(-z)$, so that the steady state solutions of Eqs. (2)–(5) $N_0(z)$ and $\mathbf{E}_0(\mathbf{r})=[0,0,E_0(z)]$ are solely functions of the $(z-)$ coordinate normal to the surface.

$$C\frac{d}{dz}\left[N_0^{-1}(z)\frac{d}{dz}(N_0^{\alpha}(z))\right]+\theta(-z)-N_0(z)=0, \tag{8}$$

$$E_0(z)=-\alpha C N_0^{\alpha-2}(z)\frac{dN_0(z)}{dz}, \tag{9}$$

with boundary conditions $N_0(-\infty)=1$ and $N_0(\infty)=0$. In addition, $N_0(z)$ and its first derivative must be continuous at $z=0$.

For $\alpha<2$ the asymptotics is nonexponential in the vacuum region.

$$N_0(z)=\begin{cases}1-A\exp\left(\dfrac{z}{\sqrt{\alpha C}}\right), & z\ll 0,\\[2ex] 2C\left(\dfrac{\alpha}{2-\alpha}\right)^2\left[\dfrac{1}{z+\zeta}\right]^{\frac{2}{2-\alpha}}, & z>0.\end{cases} \tag{10}$$

ζ,A are arbitrary constants which are fixed by the continuity of $N_0(z)$ and $E_0(z)$ at $z=0$. $\alpha=2$ seems to be another interesting case because the steady-state electron distribution leads to an exponential decay off the surface. For $\alpha>2$, there is no solution of Eq. (8).

III. LINEAR DYNAMICS

Linearization of Eqs. (2)–(6) around the steady state solution, i.e., $N(\mathbf{r},t)=N_0+N_1$, $\mathbf{E}(\mathbf{r},t)=\mathbf{E}+E_1$, and $\mathbf{J}_1(\mathbf{r},t)=N_0\mathbf{V}_1$ yields

$$\frac{\partial\mathbf{J}_1(\mathbf{r},t)}{\partial t}=-N_0(z)\mathbf{E}_1(\mathbf{r},t)-N_1(\mathbf{r},t)\mathbf{E}_0(z)-\mathrm{grad}\,P_1(\mathbf{r},t), \tag{11}$$

$$\frac{\partial N_1(\mathbf{r},t)}{\partial t}=-\mathrm{div}\,\mathbf{J}_1(\mathbf{r},t), \tag{12}$$

$$\mathrm{div}\,\mathbf{E}_1(\mathbf{r},t)=-N_1(\mathbf{r},t)+N_{ext}(\mathbf{r},t),\quad \mathrm{curl}\,\mathbf{E}_1(\mathbf{r},t)=0, \tag{13}$$

where $P_1(\mathbf{r},t)=f(z)N_1(\mathbf{r},t)$ with $f(z)=\alpha C N_0^{\alpha-1}(z)$. We are looking for a self sustaining (i.e., $N_{ext}=0$) plane wave solution propagating parallel to the surface, $N_1(\mathbf{r},t)=N_1(z)\exp[i(qx-\omega t)]$ etc. where the amplitude functions $N_1(z)$ etc. obey

$$\nabla P_1(z)=i\omega\mathbf{J}_1(z)-N_0(z)\mathbf{E}_1(z)-N_1(z)\mathbf{E}_0(z), \tag{14}$$

$$\nabla\cdot\mathbf{J}_1(z)=i\omega N_1(z), \tag{15}$$

$$\nabla\cdot\mathbf{E}_1(z)=-N_1(z),\quad \nabla\times\mathbf{E}_1(z)=0, \tag{16}$$

where $\nabla=(iq,0,\partial/\partial z)$.

Following Eguiluz *et al.*,[8] the surface plasmon dispersion can be obtained in the small q limit by first taking the divergence of Eq. (14) and then eliminating $\nabla\cdot\mathbf{J}_1$ by Eq. (15).

$$\omega^2 N_1(z)=\frac{d}{dz}\left[N_0(z)\frac{d\phi_1(z)}{dz}\right]-q^2N_0(z)\phi_1(z)-\frac{d}{dz}[E_0(z)N_1(z)]-\left(\frac{d^2}{dz^s}-q^2\right)[f(z)N_1(z)], \tag{17}$$

where $E_1=-\nabla\phi_1$. Next, $\phi_1(z)$ is represented in terms of the Green-function of the Poisson equation

$$\phi_1(z)=-\frac{1}{2q}\int_{-\infty}^{+\infty}e^{-q|z-z'|}N_1(z')dz'. \tag{18}$$

In a second step, we integrate Eq. (17) and perform a partial integration of the term $N_0(z)\phi_1(z)$ with respect to the exponential function. As a result an expansion up to first order in q yields

$$\omega_{sp}^2(q)=\frac{1}{2}+\frac{1}{2}\frac{\langle(z-z')N_1(z')\rangle}{\langle N_1(z')\rangle}q+O(q^2), \tag{19}$$

where

$$\langle f(z,z')\rangle=\int\int_{-\infty}^{+\infty}f(z,z')\left[-\frac{dN_0(z)}{dz}\right]dzdz'. \tag{20}$$

Thus, $\omega_{sp}(0)=1/\sqrt{2}$. The slope of the dispersion curve, however, is affected by the electronic surface density profile and becomes negative if $N_0(z)$ (for $q\to 0$) leaks considerably outside the geometrical surface. This result is a special

case of an important observation by Feibelman[2] that the response of the surface could be characterized by the centroid of the induced charge density. Equation (19) holds only for monopole surface plasmons for which $\langle N_1(z')\rangle \neq 0$. For multipole excitations, however, $\langle N_1(z')\rangle = 0$ and $\omega_{sp}(0) = 1/\sqrt{2}$.

IV. SOLUTION OF THE EQS. (14-16)

A. Finite surface region

To solve Eqs. (14)–(16), we first eliminate the x component of $\mathbf{J}_1$ by solving Eq. (14), which is a simple algebraic equation. Then, the remaining four linear differential equations are cast in matrix form

$$\frac{d}{dz}\mathbf{F}\Psi = \mathbf{M}\Psi, \tag{21}$$

where $\Psi(z)$ is a column vector containing $E_{1x}, E_{1z}, J_{1z}, N_1$. $\mathbf{F}$ is a diagonal matrix with entries $1,1,1,f(z)$ in the diagonal, and

$$\mathbf{M}(z) = \begin{pmatrix} 0 & iq & 0 & 0 \\ -iq & 0 & 0 & -1 \\ -\dfrac{q}{\omega}N_0(z) & 0 & 0 & i\left[\omega - \dfrac{q^2}{\omega}f(z)\right] \\ 0 & -N_0(z) & i\omega & -E_0(z) \end{pmatrix}. \tag{22}$$

Instead of using the correct self-consistent electron profiles it is convenient first to consider the following model density profiles with a finite surface region $-a<z<b$ with

$$N_0(z) = \begin{cases} 1, & z<-a \\ 0, & z>b \end{cases} \tag{23}$$

and a (continuous) interpolation in between.

For $z<-a$ the solution is

$$\Psi_1^{(-)}(z) = A_1 \begin{pmatrix} 1 \\ -i \\ -1/\omega \\ 0 \end{pmatrix} e^{qz}, \quad \Psi_2^{(-)}(z) = A_2 \begin{pmatrix} iq \\ \gamma \\ -i\omega\gamma \\ q^2-\gamma^2 \end{pmatrix} e^{\gamma z}, \tag{24}$$

where $\gamma^2 = (1-\omega^2)/f + q^2$ and $f = \alpha C$.

For $z>b$ a consistent solution requires $N_1 \equiv 0$, $J_{1z} \equiv 0$, i.e.,

$$\Psi_1^{(+)}(z) = B_1 \begin{pmatrix} 1 \\ i \\ 0 \\ 0 \end{pmatrix} e^{-qz}. \tag{25}$$

A_1, A_2, B_1 are constants that are fixed by the requirement of continuity of E_x, E_z, and J_{1z} at $z=-a,b$.

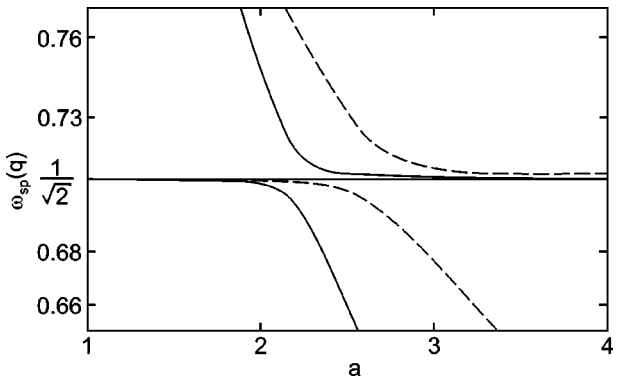

FIG. 1. Dispersion of the fundamental and first excited surface plasmon mode at $q=10^{-3}$ as a function of surface width ($b=a$). Full lines: linear interpolation, dashes lines: quadratic interpolation. Note, the change of the monopole/dipole character of the modes near $a \approx 2.5$.

To describe the steady state density profile in the surface region linear,[6] multistep,[7] and exponential[10] approximations have been used in the literature. In our first calculations we used linear and quadratic interpolations of $N_0(z)$ between $N_0(z<-a)=1$ and $N_0(z>a)=0$. For $|z|<a$, the quadratic interpolation sets $N_0(z) = \Theta(-z) + squ(z)(|z|-a)^2/2a^2$. For both types of interpolations we choose $C=\frac{1}{3}$, $\alpha=1$, and set $f(z)=\text{const}=C\alpha$. Results are shown in Figs. 1 and 2. In our next series of calculations we approximately incorporate

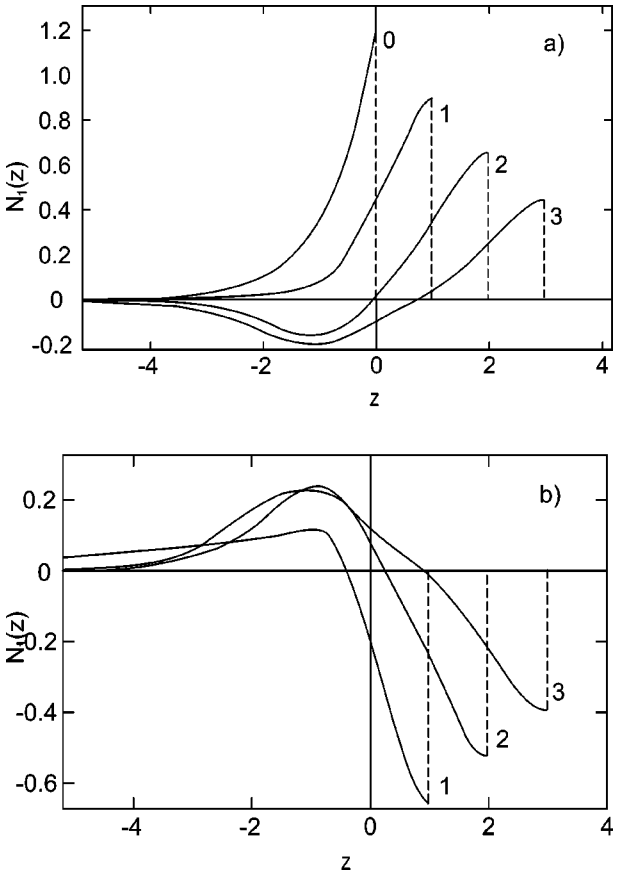

FIG. 2. Density amplitudes of the fundamental (a) and first excited (b) surface plasmon modes. Linear interpolation between $(-a,a)$ with $a=0,1,2,3$.

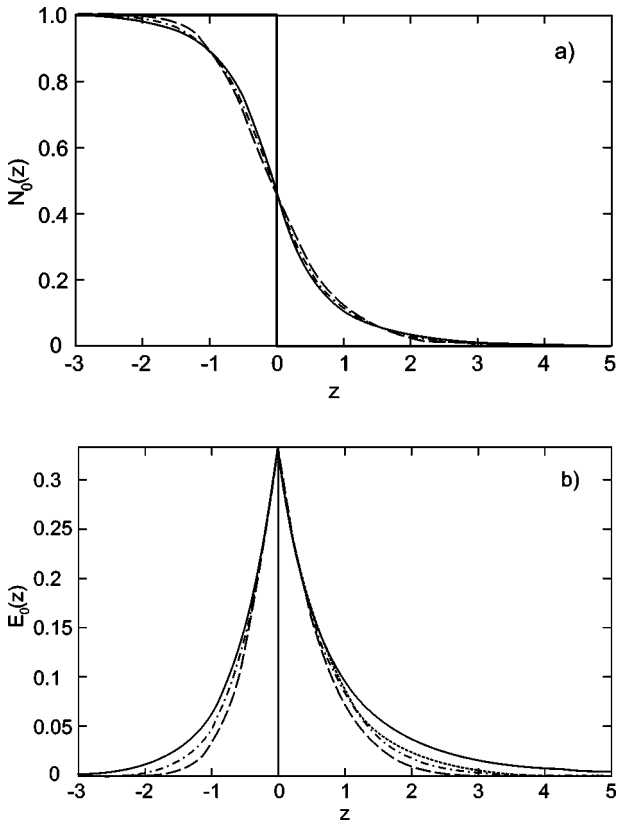

FIG. 3. Exact (solid lines) and approximated surface density profile (a) and electric field (b) for different surface width parameters: $(a,b)=(2,3)$, $(3,4)$, and $(3,5)$ (dashed, dashed–dot, and dotted lines).

the results for $N_0(z)$, $E_0(z)$ from Eqs. (8)–(9) to produce a nearly self-consistent solution for the linear response. This is done by introducing a ''window function''

$$w(z)=\begin{cases} w_<(z)=1-3(z/a)^2-2(z/a)^3, & -a<z<0 \\ w_>(z)=1-3(z/b)^2+2(z/b)^3, & 0<z<b \end{cases}, \tag{26}$$

so that the approximated field and density smoothly join their left- and right-side values,

$$E_0(z)\to\hat{E}_0(z)=E_0(z)w(z), \tag{27}$$

$$N_0(z)\to\hat{N}_0(z)=\theta(-z)-\frac{d\hat{E}_0(z)}{dz}. \tag{28}$$

Outside $-a<z<b$ we set $w(z)=0$. This procedure fixes the density and field at $z=0$ and retains charge conservation. Results are shown in Fig. 3, where $C=\frac{1}{5}$, $\alpha=\frac{5}{3}$. For numerical convenience we additionally approximate $f(z)$ by $C\alpha=\frac{1}{3}$, which would be exact if $\alpha=1$, e.g., Bennet.[6]

In the surface region, the solutions $\Psi_1^{(-)}(z)$ and $\Psi_2^{(-)}(z)$ are propagated numerically from $z=-a$ to $z=b$ by using the MATHEMATICA Routine NDSolve. The matching conditions at $z=a,b$ yield a homogeneous system of three equations. Equating its determinant to zero yields the surface plasmon dispersion which is plotted in Fig. 4.

For comparison the Ritchie-solution[1,9] for an abrupt surface profile, $a=b=0$, is given explicitly

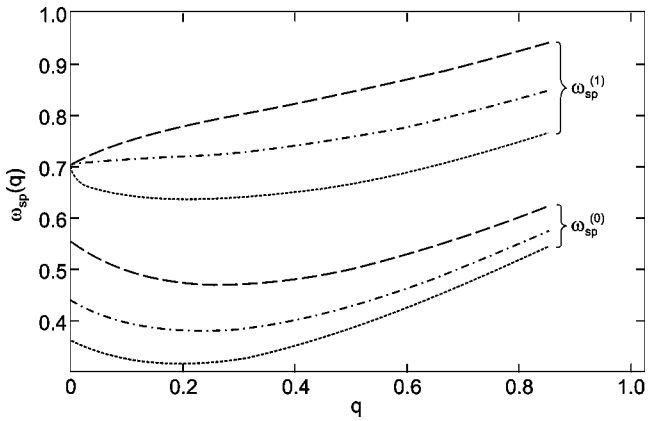

FIG. 4. Dispersion of the fundamental $\omega_{sp}^{(0)}(q)$ and first excited $\omega_{sp}^{(1)}(q)$ surface plasmon modes. Note, the dipole mode lies below the monopole mode. Parameters as in Fig. 3.

$$\omega_{sp}(q)=\sqrt{\frac{1}{2}[1+q\sqrt{2f+f^2q^2}+fq^2]}$$

$$=\frac{1}{\sqrt{2}}+\frac{1}{2}\sqrt{f}q+O(q^2), \tag{29}$$

$$N_1(z)=A_2(\gamma^2-q^2)e^{\gamma z}\theta(-z). \tag{30}$$

Note, $N_1(z)$ has a discontinuity at $z=b$. Moreover, the dispersion, Fig. 4, strongly depends on the chosen width of the surface density profile although these differences can be hardly seen in Fig. 3(a). Table I illustrates the dependence of the (negative) slope of the dispersion and decreasing $\langle N_1\rangle$ with increasing surface width. The amplitudes of the density and current density are displayed in Figs. 5 and 6.

B. Unrestricted surface region

To investigate the asymptotic behavior of Eq. (21) we first eliminate $N_1(z)$, $J_{1z}(z)$ in favor of the induced potential $\Phi(z)$, $\mathbf{E}_1=-\nabla\Phi$ which obeyes a 4th-order differential equation

$$\frac{d^2}{dz^2}\left\{f(z)\left[\frac{d^2\Phi(z)}{dz^2}-q^2\Phi(z)\right]\right\}+\frac{d}{dz}\left\{E_0(z)\left[\frac{d^2\Phi(z)}{dz^2}-q^2\Phi(z)\right]-N_0(z)\frac{d\Phi(z)}{dz}\right\}+q^2N_0(z)\Phi(z)-[q^2f(z)-\omega^2]\left(\frac{d^2\Phi}{dz^2}-q^2\Phi\right)=0. \tag{31}$$

TABLE I. Surface plasmon frequency at $q=10^{-7}$ and average density amplitude for different surface width parameters. Solutions are normalized according to $||N_1||=\int|N_1(z)|dz=1$. Note the correlation between $|<N_1>|\ll 1$ and $\omega_{sp}(0)\neq 1/\sqrt{2}$.

a	b	$\omega_0(q)$	$\langle N_1^0(z')\rangle$	$\omega_1(q)$	$\langle N_1^1(z')\rangle$
2	3	0.55557927	-0.02385037	0.70710686	-0.37521987
3	4	0.43794554	-0.00315129	0.70710680	-0.37431808
3	5	0.35942446	-0.00207955	0.67450302	-0.00662568

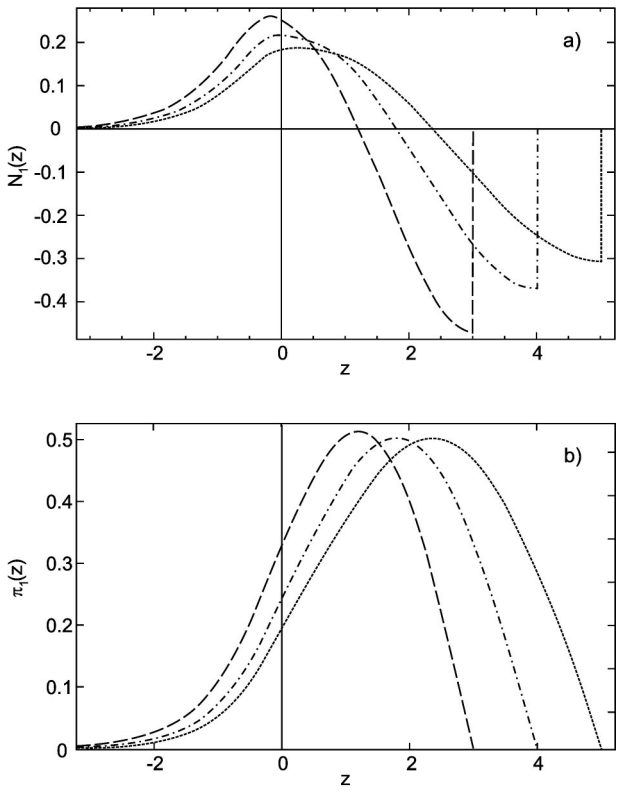

FIG. 5. Density (a) and polarization $\Pi_z = J_{1z}/i\omega$ (b) for the fundamental surface plasmon mode $\omega_{sp}^{(0)}(q)$. $q = 10^{-7}$, other parameters as in Fig. 3.

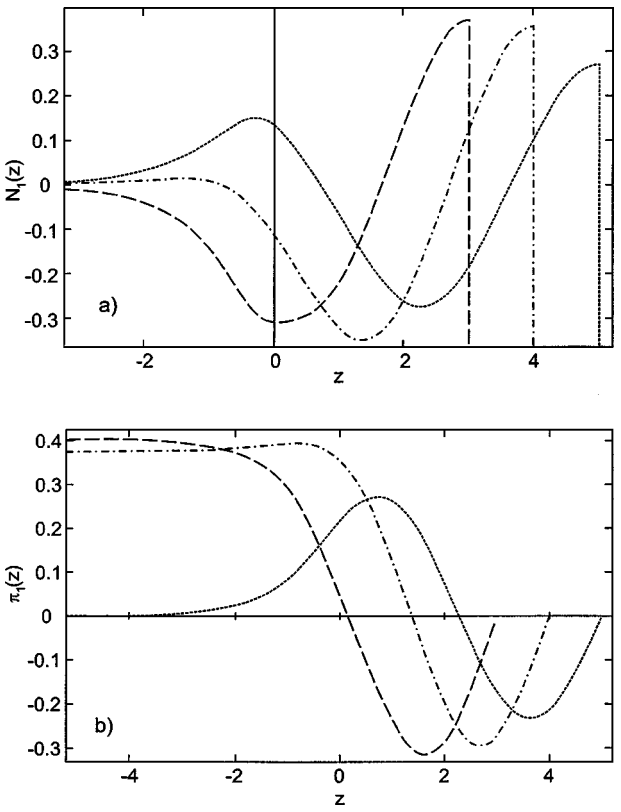

FIG. 6. Density (a) and polarization $\Pi_z = J_{1z}/i\omega$ (b) for the first exited surface plasmon mode $\omega_{sp}^{(1)}(q)$. $q = 10^{-7}$, other parameters as in Fig. 3.

As a check, we convince ourselves that the bulk plasmon dispersion is correctly described by Eq. (31). Under homogeneous conditions $N_0(z) = 1$, $E_0(z) = 0$, $f(z) = \text{const.}$, which implies $\Phi(z) = \text{const}$. Hence,

$$\omega_{bp}(q) = \sqrt{1 + fq^2} = 1 + \frac{1}{2} fq^2 + O(q^4). \tag{32}$$

Equation (32) agrees with Eq. (7) for small wavenumbers. With a bit more algebra, the Ritchie solution Eq. (29) is reproduced, too.

For $z > 0$ the differential Eq. (31) possesses a strong singularity at $z = \infty$ with characteristic index 4.[27] Asymptotically, its solution can be represented as a Thomé normal series

$$\Phi^{(+)}(z) = e^{P(z)} z^{-r} \sum_{j=0}^{\infty} c_j z^{-j}. \tag{33}$$

For the special case $\alpha = 5/3$, we get $r = 0$ and $P(z)$ is a polynomial of (maximum) degree 3. With this ansatz all four independent solutions with polynomials $P^{(1)}(z) = -qz$, $P^{(2)}(z) = qz$, $P^{(3)}(z) = i\omega z^3/10\sqrt{3}$, and $P^{(4)}(z) = -P^{(3)}(z)$ can be found.[28] However, the only solution that fulfills the boundary condition belongs to $P^{(1)}(z)$

$$\Phi^{(+)}(z) = B_1 e^{-qz} \left[1 + \frac{100}{\omega^2} \sum_{j=6}^{10} (-1)^j \frac{(j-1)!}{4!(2q)^{j-6}} z^{-j} + \ldots \right]. \tag{34}$$

The other quantities $E_x(z)$, $E_z(z)$, $N_1(z)$, and $J_{1z}(z)$ can be simply derived from Eq. (21).

Analogous to the previous study of a finite surface profile we propagate the vacuum solution Eq. (34) from a given starting point $z_2 > 0$ down to $z = 0$ where it is matched to $\Phi^{(-)}(0)$ and its derivative in terms of Eq. (24) when propagated from $z_1 < 0$ towards $z = 0$. This procedure fixes A_1 and A_2 as function of ω. ($B_1 = 1$ without loss of generality). Next, the surface plasmon eigenfrequencies are determined by the requirement of continuity of both $J_{1z}(z)$ and $N_1(z)$. Note, $z = 0$ is an inner point of the z interval so that the density must be likewise continuous. Within numerical accuracy, however, $J_{1z}(0)$ and $N_1(0)$ match within different frequency intervals, Figs. 7(a) and 7(b). Our broad–minded error estimates include numerical errors by the mathematica routine NDSolve as well as systematic errors using finite starting points at $z_1 < 0, z_2 > 0$ when extrapolating to infinity. Therefore, as already expected, for the unbounded surface region no solution exists which fulfills the required boundary conditions. For $\alpha = 2$, the situation becomes even worse and probably no bounded solution exists in $z > 0$.

V. CONCLUSIONS

During the past three decades a hydrodynamic description has served as a popular and simple model to describe the collective excitations in the bulk and at the surface of metallic systems or degenerate semiconductors. Although such a

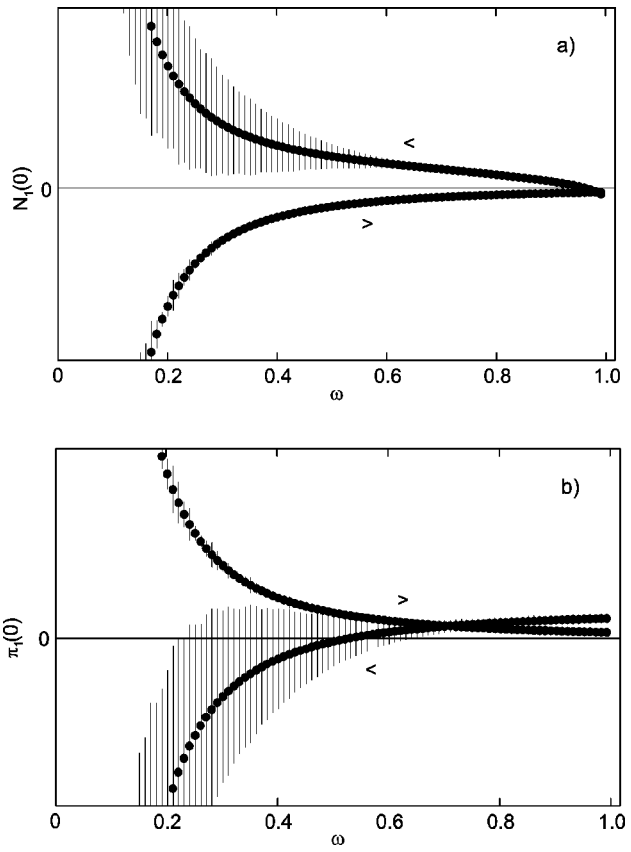

FIG. 7. Density (a) and polarization $\Pi_z = J_{1z}/i\omega$ at $z=0$ (b) as calculated numerically from the vacuum ($>$) and metal ($<$) region as a function of frequency. Error bars give large scale estimates of the numerical and systematic errors. There is no frequency, where both $N_1(0)$ and $\Pi_z(0)$ [i.e., $J_{1z}(0)$] can be continuously matched.

model cannot give a fundamental description of the (negative slope of the) surface plasmon dispersion or the existence of an extra peak in the photoemission just below ω_p they can readily fit to it (as stated by Schwartz and Schaich.[12]) Nevertheless, fitting experimental data to a surface profile gives little insight in its true shape. Although the extreme sensitity of the surface plasmon dispersion on the approximation of the ''spill-out'' of the electronic charge density across the surface was already stated by Ahlqvist and Apell[11] and Schwartz and Schaich[12] its mathematical origin was not revealed.

There are two key points which are responsible for the mathematical asymmetry of the solution with respect to the metal and vacuum regions: (a) There are two fundamental solutions in the metal but only one in the vacuum which obey the boundary conditions for the electric field at infinity. (b) For a finite surface layer not only the exponentially decaying solution but also the two oscillating modes of Eq. (21), which belong to $P^{(3,4)}(z)$ of Eq. (31) come into play. Then, unavoidably, a jump in the density at the vacuum side of the boundary arises, which is clearly seen in Figs. 5(a) and 6(a). Nevertheless, this is physically acceptable if the jump is located very close to the surface as e.g. in the Ritchie–solution (30). Such a discontinuity mimics the strong decrease of the electronic density near the surface, which is caused by the electronic work function. However, a discontinuity in the electronic density away from the real surface must be considered as a severe approximation error. With increasing surface widths the solution does not tend to zero and the linearized equations become invalid – yet the surface plasmon dispersion changes in the correct fashion, if $a,b \ll 1$. For an unrestricted vacuum region a consistent treatment additionally requires $N_1(+\infty)=0$, which rules out the two oscillating solutions so that the matching conditions cannot be fulfilled. In mathematical terms, the HD model defines an ill–posed problem and the finite surface layer model is not a well defined approximation of the infinite system-neither for the monopole nor for the multipole surface excitations.

The origin of this flaw lies in the fact that in the vacuum the electronic state is described by quantum mechanics rather than by the HD model, i.e. the grad$P$ term becomes less important (or perhaps meaningless). Instead, the (sofar forgotten) finite work function of the metal enforces an exponential decay of the density and current density in the vacuum region. This behavior can be simulated by adding a constant term E_W to $E_0(z)$ in Eqs. (21) and (22). Provided the spill–out of the electronic charge is small [$N_0(z)\approx 0$, $E_0(z)\approx 0$ for $z>0$], we obtain a second solution, which is linear independent of Eq. (25)

$$\Psi_2^{(+)}(z) = B_2 \begin{pmatrix} Kq \\ iK^2 \\ \omega(K^2-q^2) \\ iK(K^2-q^2) \end{pmatrix} e^{-Kz}. \tag{35}$$

$K \approx \omega_{sp}/E_W \approx 2\sqrt{2mW/\hbar^2}$, W is the work function of the metal. Now, a continuous matching of Ψ^+ with Ψ^- is possible. As a result, we obtain for the surface plasmon dispersion coefficient, Eq. (1)

$$c_{sp} = \frac{1}{2\sqrt{2}} \frac{2f_b K^2 - 1}{\sqrt{2f_b}K^2 + K}, \tag{36}$$

where $f_b = \alpha C$ is the bulk value of f which is related to the bulk plasmon dispersion coefficient, Eq. (32), by $f_b = 2c_b$. For $K \to \infty$ the Ritchie–solution Eq. (30) is obtained. If K is sufficiently small, c_s becomes negative. For sodium and potassium, however, this estimate seems to be too crude and does not lead to a negative value of the surface plasmon dispersion coefficient.

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