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Plasmon excitation by charged particles interacting with metal surfaces

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Abstract

Recent experiments (R.A. Baragiola and C.A. Dukes, Phys. Rev. Lett. 76 (1996) 2547) with slow ions incident at grazing angle on metal surfaces have shown that bulk plasmons are excited under conditions where the ions do not penetrate the surface, contrary to the usual statement that probes exterior to an electron gas do not couple to the bulk plasmon. We here use the quantized hydrodynamic model of the bounded electron gas to derive an explicit expression for the probability of bulk plasmon excitation by external charged particles moving parallel to the surface. Our results indicate that for each q (the surface plasmon wave vector) there exists a continuum of bulk plasmon excitations, which we also observe within the semi-classical infinite-barrier (SCIB) model of the surface. © 1999 Elsevier Science B.V. All rights reserved.

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It is well known that charged particles interacting with solid surfaces can create electronic collective excitations in the solid. These are bulk [1] and surface [2] plasmons. In the absence of electron-gas dispersion, the scalar electric potential due to bulk plasmons vanishes outside the surface [3]; hence, in this case probes exterior to the solid can only generate surface excitations. That electron-gas dispersion allows external probes to interact with bulk plasmons was discussed by Barton [4] and Eguiluz [5], and more recently by Nazarov and Luniakov ¹ [6]. Nevertheless, the fact that within a non-local description of screening bulk plasmons do give rise to a potential outside the solid has been ignored over the years [7,8], even when electron-gas dispersion has been

included; also, current non-local theories of plasmon excitation by external charges have not shown evidence for bulk plasmon excitation outside the solid ² [8–10]. Recently, Baragiola and Dukes [11] have studied the emission spectra produced by slow ions

¹ We note that ordinary conditions of continuity of potential and normal component of displacement vector at boundaries are applied in this paper, and we believe there is little rationale for such a procedure when imputing wavevector-dependent dielectric functions to adjoining media.

² It is argued in this paper that the bulk plasmon feature of Fig. 1 is not due to excitation and decay of a bulk plasmon, thereby bulk plasmons being only able to compete with surface plasmons when the ion is entering the metal.

that were incident at grazing angle; their data indicate that the bulk plasmon is importantly involved in the emission process, though the projectiles are not expected to have penetrated into the solid. Bulk plasmon excitation in electron emission spectra produced by slow multiply charged ions has also been investigated [12], with projectiles that may enter the solid.

In this Letter we derive, within the quantized hydrodynamic model of the bounded electron gas [13], an explicit expression for the probability of bulk plasmon excitation by external charged particles moving parallel to a jellium surface. Our model, which assumes a sharp electron density profile at the surface, neatly displays the role of bulk plasmon excitations in the interaction of charged particles moving near a metal surface. We also demonstrate that our results for the total energy-loss probability agree with standard calculations [14] derived either by solving the linearized Bloch hydrodynamic equations [15] or within the semi-classical infinite-barrier (SCIB) model of the surface [16,17] with the hydrodynamic approximation for the bulk dielectric function. Though it has been generally believed that when charged particles move outside the solid the energy loss predicted in these models is fully described by the excitation of surface plasmons [8], we demonstrate that for each \mathbf{q} (the surface plasmon wave vector) excitation of both a discrete surface plasmon and a continuum of bulk plasmons contribute to the total energy-loss probability, in agreement with the prediction of our quantized hydrodynamic scheme.

Take an inhomogeneous electron system capable of self-oscillations about a ground state described by density-functional theory (DFT) [18]. In the hydrodynamic limit [19] the system is characterized by the electron density $n(\mathbf{r}, t)$ and a velocity field $\mathbf{u}(\mathbf{r}, t)$. The total energy of the system can then be expressed as [20] (we use atomic units throughout, i.e., $e^2 = \hbar = m_e = 1$)

$$H = G[n(\mathbf{r}, t)] + \int d\mathbf{r} n(\mathbf{r}, t) \left[\frac{1}{2} |\nabla\psi|^2 - V_0 - V_1 \right] + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r}, t)n(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|}, \quad (1)$$

where irrotational flow has been assumed, i.e., $\mathbf{u}(\mathbf{r}, t) = -\nabla\psi$, and retardation effects have been neglected. $G[n(\mathbf{r}, t)]$ represents the exchange, correlation and internal kinetic energies of the electron system. V_0 is the electrostatic potential due to the neutralizing ionic background of density n_0 , and V_1 represents the external perturbation. From Eq. (1) the basic hydrodynamic equations can be derived, following Bloch's approach [19], and they can be linearized in the deviation $n - n_0$ from the equilibrium value to find the existence of self-sustaining normal modes of oscillation.

We consider a charged particle moving with velocity \mathbf{v} outside of a metallic surface, along a trajectory that is parallel to the surface, with a classical charge distribution given at $\mathbf{r} = (\mathbf{r}_{\parallel}, z)$ by $\rho_{\text{ext}}(\mathbf{r}, t) = Z_1 \delta(\mathbf{r}_{\parallel} - \mathbf{v}t) \delta(z - z_0)$. We represent the ionic background by a jellium model (the jellium occupying the half-space $z < 0$), and assume a sharp electron density profile at the surface. We also neglect exchange-correlation contributions to $G[n]$, and approximate it by the Thomas-Fermi functional [19]. In this approximation, for each value of \mathbf{q} (the wave vector parallel to the surface) there exist both bulk and surface normal modes of oscillation with frequencies given by the following dispersion relations [13]:

$$(\omega_{q,p}^B)^2 = \omega_p^2 + \beta^2(q^2 + p^2) \quad (2)$$

and

$$(\omega_q^S)^2 = \frac{1}{2} \left[\omega_p^2 + \beta^2 q^2 + \beta q (2\omega_p^2 + \beta^2 q^2)^{1/2} \right], \quad (3)$$

respectively, where $\omega_p = (4\pi n_0)^{1/2}$ is the so-called plasma frequency and β represents the speed of propagation of hydrodynamic disturbances in the electron system. We choose $\beta = \sqrt{3/5} q_F$, q_F being the Fermi momentum³.

Now we follow Ref. [13] to quantize, after linearization, the hamiltonian of Eq. (1) on the basis of

³ While use of the Thomas-Fermi $G[n]$ functional, which assumes static screening, predicts $\beta = \sqrt{1/3} q_F$, the value $\beta = \sqrt{3/5} q_F$ is expected to be appropriate when high frequencies of the order of the plasma frequency are involved [1].

the normal modes corresponding to Eqs. (2) and (3), which we shall refer after quantization as bulk and surface plasmons, respectively. We find

$$H = H_G + H_0^B + H_0^S + H_1^B + H_1^S, \quad (4)$$

where H_G represents the Thomas-Fermi ground state of the static unperturbed electron system [19]. H_0^B and H_0^S are free bulk and surface plasmon hamiltonians:

$$H_0^B = \frac{1}{\Omega} \sum_{q,p>0} [1/2 + \omega_{q,p}^B] a_{q,p}^\dagger(t) a_{q,p}(t) \quad (5)$$

and

$$H_0^S = \frac{1}{A} \sum_q [1/2 + \omega_q^S] b_q^\dagger(t) b_q(t), \quad (6)$$

where Ω and A represent the normalization volume and the normalization area of the surface, respectively, and where $a_{q,p}(t)$ and $b_q(t)$ are Bose-Einstein operators that annihilate bulk and surface plasmons with wave vectors (q,p) and q , respectively. $H_1^{B/S}$ are contributions to the hamiltonian coming from the coupling between the external particle and bulk/surface plasmon fields:

$$H_1^{B/S} = \int d\mathbf{r} \rho_{\text{ext}}(\mathbf{r},t) \phi^{B/S}(\mathbf{r},t), \quad (7)$$

$\phi^{B/S}(\mathbf{r},t)$ representing operators corresponding to the scalar electric potential due to bulk/surface plasmons. Outside the metal ($z > 0$),

$$\begin{aligned} \phi^B(\mathbf{r},t) = & -\frac{1}{\Omega} \sum_{q,p>0} f_{q,p}^B(z) e^{iq \cdot \mathbf{r}_\parallel} [a_{q,p}^\dagger(t) \\ & + a_{-q,p}(t)] \end{aligned} \quad (8)$$

and

$$\phi^S(\mathbf{r},t) = -\frac{1}{A} \sum_q f_q^S(z) e^{iq \cdot \mathbf{r}_\parallel} [b_q^\dagger(t) + b_{-q}(t)], \quad (9)$$

where $f_{q,p}^B(z)$ and $f_q^S(z)$ are bulk and surface coupling functions, respectively:

$$\begin{aligned} f_{q,p}^B(z) &= \frac{\sqrt{2\pi/\omega_{q,p}^B} \omega_p p e^{-qz}}{[p^4 + p^2(q^2 + \omega_p^2/\beta^2) + \omega_p^4/(4\beta^4)]^{1/2}} \end{aligned} \quad (10)$$

and

$$f_q^S(z) = \frac{\sqrt{\pi\gamma_q/\omega_q^S} \omega_p}{[q(q + 2\gamma_q)]^{1/2}} e^{-qz}, \quad (11)$$

and where γ_q represents the so-called inverse decay length of surface plasmon charge fluctuations [5]:

$$\gamma_q = \frac{1}{2\beta} \left[-\beta q + \sqrt{2\omega_p^2 + \beta^2 q^2} \right]. \quad (12)$$

We derive the potential induced by the presence of the external perturbing charge as the expectation value of the total scalar potential operator [21]:

$$V^{\text{ind}}(\mathbf{r},t) = \frac{\langle \Psi_0 | \phi_H^B(\mathbf{r},t) + \phi_H^S(\mathbf{r},t) | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle}, \quad (13)$$

where $|\Psi_0\rangle$ is the Heisenberg ground state of the interacting system and where $\phi_H^B(\mathbf{r},t)$ and $\phi_H^S(\mathbf{r},t)$ are the operators of Eqs. (8) and (9) in the Heisenberg picture. Our results [22] reproduce previous calculations for the image potential (defined as half the induced potential at the position of the charged particle that creates it) of a static ($v = 0$) external charged particle [5], which in the case of a non-dispersive electron gas ($\beta = 0$) coincides with the classical image potential [23] $V_{\text{im}}(z) = -(4z)^{-1}$.

The energy loss per unit path length of a moving charged particle can be obtained as the retarding force that the polarization charge distribution in the electron gas exerts on the projectile itself [24]:

$$-\frac{dE}{dx} = \frac{1}{v} \int d\mathbf{r} \rho_{\text{ext}}(\mathbf{r},t) \nabla V^{\text{ind}}(\mathbf{r},t) \cdot \mathbf{v}. \quad (14)$$

By introducing here the induced potential, which we evaluate from Eq. (13) up to first order in Z_1 , we find ⁴

$$-\frac{dE}{dx} = \frac{1}{v} \int_0^{q_c} dq \int_0^{qv} d\omega \omega [P_{q,\omega}^B + P_{q,\omega}^S], \quad (15)$$

where $P_{q,\omega}^{B/S}$ represent probabilities per unit time, unit wave number and unit frequency for the excitation of bulk/surface plasmons with wave number q and frequency ω :

$$P_{q,\omega}^B = Z_1^2 \frac{q}{2\pi^2} \int_0^\infty dp \frac{\omega_{q,p}^B [f_{q,p}^B(z_0)]^2}{\sqrt{q^2 v^2 - \omega^2}} \delta(\omega - \omega_{q,p}^B) \quad (16)$$

and

$$P_{q,\omega}^S = Z_1^2 \frac{q \omega_q^S [f_q^S(z_0)]^2}{\pi \sqrt{q^2 v^2 - \omega^2}} \delta(\omega - \omega_q^S). \quad (17)$$

For comparison, we note that by solving the linearized Bloch hydrodynamic equations the total probability per unit time, unit wave number and unit frequency for the external particle to transfer momentum q and energy ω to the electron gas is found as:

$$P_{q,\omega} = 2Z_1^2 \omega_p^2 \frac{\text{Im}\left\{-1/\left[\omega_p^2 - 2\beta^2 \Lambda_q (\Lambda_q + q)\right]\right\}}{\pi \sqrt{q^2 v^2 - \omega^2}} \times e^{-2qz_0}, \quad (18)$$

where

$$\Lambda_q = \frac{1}{\beta} \sqrt{\omega_p^2 + \beta^2 q^2 - \omega(\omega + i\delta)}, \quad (19)$$

and where δ is a positive infinitesimal. The same result is obtained [14] within either the specular reflection (SR) [16] or the SCIB [17] model of the surface, as long as the hydrodynamic approximation for the bulk dielectric function is considered.

Within the various semiclassical approaches leading to Eq. (18) the role played by bulk and surface plasmons goes unnoticed. Furthermore, Eq. (18) shows no evidence of losses at the bulk plasmon frequency, and it has been generally believed that the energy loss predicted by this equation originates entirely in the excitation of surface plasmons. That this is not the case is clearly shown in Fig. 1. This figure shows $P_{q,\omega}$, as computed from Eq. (18) with $\omega_p = 15.8$ eV corresponding to the bulk plasma frequency of aluminum metal and with a finite damping parameter δ accounting for the finite lifetime of plasmon fields. The parallel momentum transfer, the velocity and the distance of the particle trajectory above the surface have been taken to be $q = 0.4$ au, $v = 2$ au and $z_0 = 1.0$ au, respectively, and different values of δ have been considered. One sees that loss occurs at the surface plasmon energy ω_q^S given by Eq. (3), while a continuum of bulk plasmon excitations occurs at energies $\omega_{q,p}^B$ (see Eq. (2)), which all are over $\omega_{q,0}^B = (\omega_p^2 + \beta^2 q^2)^{1/2}$, as predicted by Eqs. (16) and (17). In the limit as $\delta \rightarrow 0^+$, both bulk and surface contributions to the total energy-loss probability of Eq. (18) exactly coincide with the predictions of Eqs. (16) and (17), thus demonstrating the full equivalence between our quantized hydrodynamic scheme and the more standard semiclassical approaches. Also, either introduction of both Eqs. (16) and (17) into Eq. (15) or replacement of the integrand in Eq. (15) by the energy-loss probability of Eq. (18) with $\delta \rightarrow 0$ result in exactly the same

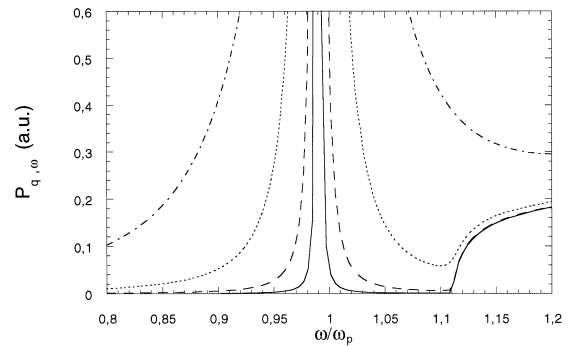


Fig. 1. Energy-loss probability of Eq. (18), as a function of ω/ω_p , with $\omega_p = 15.8$ eV, $q = 0.4$ au, $v = 2$ au, $z_0 = 1$ au, $Z_1 = 1$ and various values of the damping parameter δ : $10^{-4}\omega_p$ (solid line), $10^{-3}\omega_p$ (dashed line), $10^{-2}\omega_p$ (dotted line), and $10^{-1}\omega_p$ (dashed-dotted line).

⁴ The quantal hydrodynamic model of the electron gas assumes that infinitely long-lived plasmons are the only possible excitations for all wave vectors. Since such an approximation is no longer valid for short wavelengths where collective effects no longer occur, we use a cut-off in the momentum integration, which we choose to be $q_c \approx 2v$.

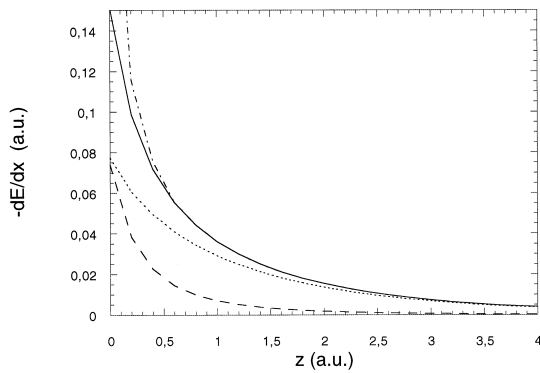


Fig. 2. Energy loss per unit path length versus the distance from the surface z_0 , as obtained from Eq. (15) with either the use of Eqs. (16) and (17) or the use of Eq. (18) and $\delta \rightarrow 0$ (solid line). Separate contributions from Eqs. (16) and (17) are represented by dashed and dotted lines, respectively. A proton ($Z_1 = 1$) is assumed to move with velocity $v = 2$ au parallel to the surface of a bounded electron gas with an electron density equal to that of aluminum ($r_s = 2.07$). The dashed-dotted line represents the total energy-loss obtained from Eq. (15) with no cut-off in the momentum integration ($q_c \rightarrow \infty$).

total energy loss. As the damping parameter increases, surface plasmon excitation broadens to energies over $\omega_{q,0}^B$, and for $\delta \approx \omega_p/10$ bulk plasmon contributions to the energy loss go unnoticed.

Fig. 2 exhibits, by a solid line, the energy loss per unit path length versus the distance z_0 from the surface, as obtained from Eq. (15). In this case a proton ($Z_1 = 1$) moves with velocity $v = 2$ au parallel to the surface of a bounded electron gas of density equivalent to that of aluminum ($r_s = 2.07$)⁵. Separate contributions from the excitation of bulk and surface plasmons are represented by dashed and dotted lines, as obtained with the use of Eqs. (16) and (17), respectively. One sees that for $z_0 < 2$ au the contribution to the energy loss from the bulk channel is important, while for larger values of z_0 the surface channel alone gives a sufficiently accurate description of the total energy loss.

Fig. 3 shows, by a solid line, results for the energy loss of Eq. (15), as a function of the velocity of the projectile, with $Z_1 = 1$, $r_s = 2.07$ and $z_0 = 1$ au. Dashed and dotted lines represent separate con-

tributions to the total energy loss from the excitation of bulk and surface plasmons, respectively. We note that for a projectile moving at $z_0 = 1$ au the contribution to the energy loss from the bulk channel is observable for all velocities, the relative importance of bulk plasmon excitations becoming more important at velocities around the plasmon threshold velocity when the projectile has enough energy to excite plasmons. For comparison, the result one obtains either from Eq. (17) or Eq. (18) in the case of a non-dispersive electron gas ($\beta = 0$), which coincides with the classical formula of Echenique and Pendry [25], is represented by a dashed-dotted line.

In conclusion, we have used the quantized hydrodynamic model of the bounded electron gas to demonstrate that bulk plasmons undergo real excitations, even in the case of charged particles that do not penetrate into the solid. We have derived explicit expressions for the probability of both bulk and surface plasmon excitation by external charged particles moving parallel to the surface, which neatly display the role that bulk plasmon excitation plays in the interaction of charged particles moving near a metal surface. The full equivalence between our quantized hydrodynamic scheme and the more standard semiclassical approaches has been demonstrated. It has been generally believed that energy loss predicted by these approaches originates entirely in the excitation of surface plasmons. However, we have shown that for each value of the wave vector parallel to the surface both a discrete surface plas-

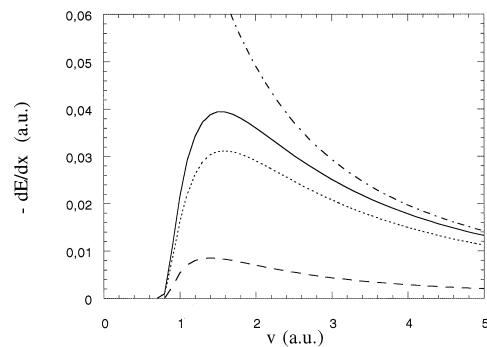


Fig. 3. As in Fig. 2, but now the energy-loss per unit path length of Eq. (15) is represented as a function of the velocity of the projectile for a given value of the distance from the surface: $z_0 = 1$ au. The dashed-dotted line here represents the result obtained in the case of a non-dispersive electron gas ($\beta = 0$).

⁵ The so-called electron-density parameter r_s is defined by the relation $1/n_0 = (4/3)\pi r_s^3$.

mon excitation and a continuum of bulk plasmon excitations contribute to the total energy-loss probability. We have also presented explicit calculations of the energy loss per unit path length of protons moving outside of a metal along a trajectory that is parallel to the surface, and our results indicate that the contribution from the bulk channel is important for all projectile velocities, as long as the distance from the surface is smaller than a few atomic units.

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