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Nonlocal theory for surface-plasmon excitation in simple metals

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A nonlocal theory based on the hydrodynamical model for an electron gas is applied to calculate the average number of surface plasmons created by a moving external point charge due to its dynamical interaction with a metal surface. In particular, quantitative estimates are provided for the effects of various parameters—including the speed of the external charge, the hydrodynamic dispersion, finite impurity broadening, and the r_s value of the metal—on the surface-plasmon excitation probability in simple metals. It is shown that, as expected, the inclusion of nonlocal dispersion corrections in the theory eliminates the infrared divergence in the surface-plasmon excitation probability that exists in the local theory for vanishing speed of the external charge. Numerical results are presented for the average number of surface plasmons excited by slow external protons interacting with the surface.

A point-charged particle outside a semi-infinite metal which is bounded in the half-space $z<0$, interacts with the metal surface through the well-known classical image-potential formula $V_{\rm im}(z)=-Q/2z$ where Q is the strength of the charge on the external particle located at the position $z>0$. In the literature, the expression "image potential" sometimes refers to the actual interaction energy between an external point charge and the surface, in which case, an additional factor of $\frac{1}{2}$ is required. We take $z=0$ to be the plane defining the metal surface and use a jellium-background model assuming complete translational invariance in the x-y plane. We also take $|e|=\hbar=m=1$ throughout this paper where e and m are, respectively, the electronic charge and mass. It is well-known[1] that the classical formula is valid only approximately, and it most certainly breaks down as $z\rightarrow 0$. In particular, finite screening in the metal, diffuseness of the surface which is not abrupt on an atomic scale, and finite velocity of the external particle—all provide some natural length scales leading to the saturation at small z of the divergent $(1/z)$ image potential of the classical formula. For large z the classical formula is valid in an asymptotic sense. In a recent paper[1] the hydrodynamical model[2] for an electron gas was applied to obtain corrections to the classical image theory, and the roles of the above three length scales in saturating the classical image potential were clarified.

The primary motivation of this paper is theoretical—we want to calculate the surface-plasmon excitation probability due to interaction with an external point charge within a nonlocal hydrodynamic (or, plasmon-pole) response formalism. We find, not unexpectedly, that just as the image potential saturates at the surface due to non local effects, the surface-plasmon excitation probability is also finite for all velocities of the external probe within our theory. Because we have introduced a number of simplifying approximations in our model (such as, the step-density approximation for the surface and the neglect of lattice effects), we refrain from making any comparison with experiment except to point out that nonlocal effects considered in this paper are quantitatively very important in situations involving interaction between the surface and heavier probe particles such as slow-moving (keV) protons. For fast-electron energy-loss spectroscopy, on the other hand, nonlocal effects are usually small and can be neglected.

In this paper we consider the problem of calculating the surface-plasmon[3,4] excitation probability as the moving external particle interacts with the metal surface through the image potential. Specifically we calculate the number of surface plasmons created in the metal as the point charge moves from very far away $(z=\infty)$ to the metal surface $(z=0)$ along a well-defined trajectory, and is reflected specularly at the surface going back to infinity again. We treat the external particle classically and take its trajectory to be normal to the metal surface—in fact we define the z axis to be the line of motion of the probe particle. We neglect recoil of the particle completely since it is not essential to our discussion. However, recoil effects can easily be incorporated within our formalism. To be specific, we also choose $Q=1$ which makes the probe particle an external electron or proton. The model chosen in this paper for the metal surface is the so-called step-density sharp surface model where the unperturbed electron density describing the metal is taken to be a Heaviside step function $n_0(z)=n_0\Theta(-z)$. More complicated surface models can be treated within the same formalism, but the algebra becomes very tedious without the emergence of any essential new physics.

We use the nonretarded hydrodynamic theory[1,5–10] to describe the linear response of the bounded electron gas (which is our model for the semi-infinite metal) to the external perturbation. The hydrodynamical model has been used[1,5–10] extensively in the study of surface collective modes in metals[5–8] and semiconductors.[10] The particular formalism we are using has been discussed in detail in Ref. 1 and will not be reproduced here.

We describe the surface plasmons by adopting the well-known normal-mode analysis in which the twodimensional wave vector $\mathbf{q}$ in the x-y plane parallel to the surface is used as a label. Then the number of surface plasmons, N_q, with a particular wave vector $\mathbf{q}$ is given by,[3,4]

$$N_q \omega_s(q) = V_q \ , \tag{1}$$

where $\omega_s(q)$ is the energy of a surface plasmon with the wave vector $\mathbf{q}$ and V_q is the total work done by the external charge in moving from $z=+\infty$ to $z=0$ and then back to $z=+\infty$ again after being reflected specularly at the surface. Note that V_q is only the total *dissipative* work done by the external charge; the conservative work is automatically canceled since it is equal and opposite during the inward and the outward paths of the motion. Obviously the conservative part of the potential energy does not participate in the creation of *real* excitations. Since the hydrodynamical response function is basically a plasmon-pole approximation to the complete response of the system, it is sensible to attribute the total potential energy as due to the collective modes in the system. Hydrodynamic approximation thus neglects the electron-hole pair excitations in the metal. The total number of surface plasmons, N, is given by summing over all the modes,

$$N = \sum_{\mathbf{q}} N_q = \sum_{\mathbf{q}} V_q / \omega_s(q) \ . \tag{2}$$

To obtain N we need an expression for the force acting on the external charge (due to the metal surface) which can then be integrated over the whole trajectory to give us the net work done by the particle. The interaction between the surface and the external charge is the image interaction which has been calculated[1] earlier in a nonlocal hydrodynamical formalism. By a direct generalization of the result in Refs. 1 and 10 we get the image potential $\phi_{\text{im}}(z,t;q)$ induced by the external charge as

$$\phi_{\text{im}}(z,t;q) = \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} e^{-i\omega t} \left[-\frac{2\pi}{q} \int_{-\infty}^{0} dz' e^{-q|z-z'|} n(z') \right] , \tag{3}$$

where $n(z')$, the induced charge density in the metal, is given by

$$n(z') \equiv n(z';q,\omega) = \frac{\omega_p^2(\gamma+q)e^{\gamma z}}{v(q+i\alpha)(\alpha\gamma^2\beta^2 + 2\gamma q\beta^2 - \omega_p^2)} + \{\alpha \to -\alpha\} \ , \tag{4}$$

with ω_p, v being respectively the plasma frequency of the metal and the velocity of the external charge, $\alpha = \omega/v$, and $\gamma = \beta^{-1}(\omega_p^2 + \beta^2 q^2 - \omega^2)^{1/2}$. The parameter β in the theory, the electronic compressibility, is responsible for nonlocal effects (in a purely local theory $\beta \equiv 0$). Equation (3) is derived by combining Euler's equation, the equation of continuity and Maxwell's equations. We also use the boundary condition that the normal current density in the metal vanishes at the surface $z=0$. The work done V_q for the qth normal mode during the whole trajectory is now given by

$$V_q = \int_{t=-\infty}^{+\infty} dt \, v(t) \frac{\partial \phi_{\text{im}}}{\partial z} \bigg|_{z=v(t)t} \tag{5}$$

The particle position is given by $z=-vt$ for $t<0$ and $z=vt$ for $t>0$. We choose the origin of time such that the particle starts from $z=+\infty$ at $t=-\infty$, moves with uniform speed v to the metal surface along the z axis, is reflected specularly at the surface (which is at $z=0$), and then moves back with uniform speed to $z=+\infty$ at $t=+\infty$. Combining Eqs. (1)–(5) we get for the surface-plasmon excitation strength

$$N = \int \frac{d^2q}{(2\pi)^2} [\omega_s(q)]^{-1} \int_{-\infty}^{+\infty} dt \, v(t) \frac{\partial}{\partial z} \left\{ \int_{+\infty}^{-\infty} \frac{d\omega}{2\pi} e^{-i\omega t} \left[-\left[\frac{2\pi}{q}\right] \int_{-\infty}^{0} dz' \exp[-q \,|\, |vt| - z' \,|\,] n(z') \right] \right\} . \tag{6}$$

It turns out that if we use Eq. (4) for the induced electron-density fluctuation then four of the five integrals in Eq. (6) can be evaluated analytically and we get (after considerable algebra),

$$N = v^2\omega_p^2 \int_0^\infty dq \frac{q^2}{[q^2v^2 + \omega_s^2(q)]^2 \omega_s(q) \{ 1 + \beta q / [3\beta^2 q^2 + 2\omega_p^2 - 2\beta q (2\omega_p^2 + \beta^2 q^2)^{1/2}]^{1/2} \}} \ , \tag{7}$$

where

$$\omega_s(q) = \left[\frac{\omega_p^2}{2} + \frac{\beta^2 q^2}{2} + \beta q \left[\frac{\omega_p^2}{2} + \frac{\beta^2 q^2}{4} \right] \right]^{1/2} , \tag{8}$$

is the surface-plasmon dispersion relation.[1,3,9] Equation (7) is the new theoretical result in this paper and it gives the average number *real* surface plasmons created by the external charge in its interaction with the metal.

In the local limit, $\beta=0$ and Eq. (8) gives

$$N \,|_{\beta=0} = v^2\omega_p^2 \int_0^\infty dq \frac{q^2}{(q^2v^2 + \omega_p^2/2)^2(\omega_p/\sqrt{2})} = \frac{\pi}{2v} \ . \tag{9}$$

Equation (9) is the well-known[3,4] result for the surface-plasmon excitation probability in a local theory which was derived[3,4] a long time ago. The fundamental conceptual problem of the local theory is its infrared singularity which predicts that the number of surface excitations diverges as $v \rightarrow 0$. This infrared divergence is corrected in our nonlocal theory, since the low-velocity limit of Eq. (8) is zero:

$$N(v \rightarrow 0)\,|_{\beta \neq 0} = O(v^4)\ . \tag{10}$$

Equation (10) is intuitively appealing since nonlocality in the response should cut off the infrared divergence for $v < \beta$, the nonlocal theory [Eq. (7)] reduces to the local result [Eq. (9)] as it must.

In Fig. 1 we show the surface-plasmon excitation probability N plotted against the velocity v of the external charge (with v being measured in units of v_F, the Fermi velocity of the metal) for a fixed metallic electron density characterized by $r_s = 3.0$ where $r_s^3 = (3/4\pi n_0 a_B^3)$, with a_B as the Bohr radius, is the standard dimensionless number which is used to parametrize metallic free-electron densities. As one can see from the figure, nonlocal effects become important for $v \lesssim v_F$ and the surface-plasmon excitation probability goes down for small v. For large v, N falls off as v^{-1}. We have chosen $\beta^2 = v_F^2/3$ for this figure which is the standard hydrodynamic compressibility. Changing β to $\beta^2 = 3v_F^2/5$ [so as to reproduce the random-phase-approximation (RPA) bulk-plasmon dispersion relation[1,9]] makes insignificant change in the depicted result.

Since recoil of the external probe has been neglected in our theory, it is more appropriate to consider external probes with very high energy ($E \gg E_F$, ω_p) so that the neglect of recoil is a good approximation. We can do that by taking the external probe particles to be protons which have high kinetic energy ($\sim$ keV range) for the velocity range of Fig. 1. In Fig. 2 we show (for a fixed

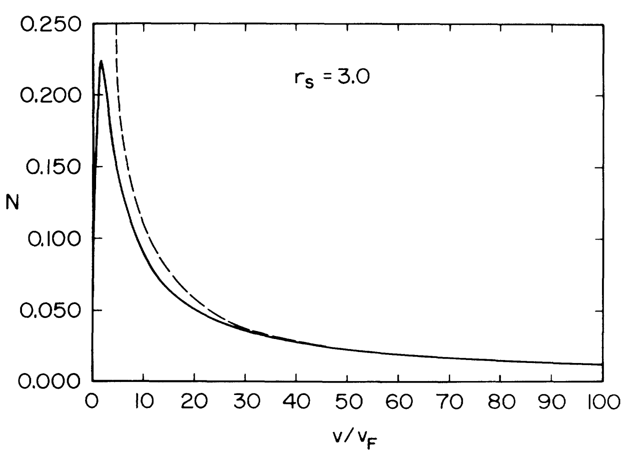

FIG. 1. Shows the average number of surface-plasmon excitations as a function of the velocity (v) of the external probe with the velocity measured in units of v_F, the Fermi velocity of the metal (solid line, hydrodynamic nonlocal result; dashed line, local result). For $v/v_F \gtrsim 10$ local results are very close to the nonlocal curve.

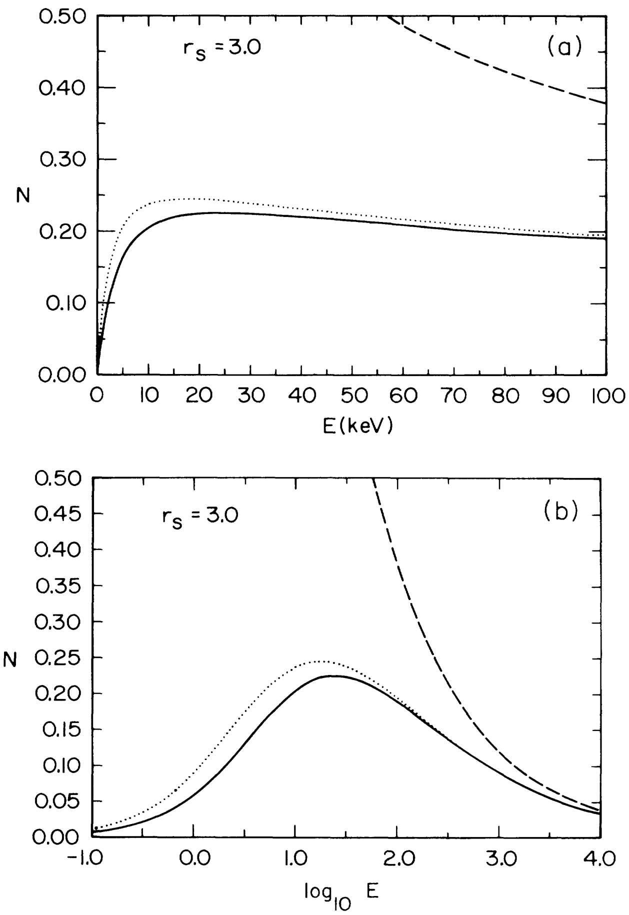

FIG. 2. Shows the average number of surface plasmons (in metal with $r_s = 3.0$) excited by external protons with energy E in keV. Three different approximations are shown: Plasmon-pole (solid-line), hydrodynamic (dotted line), and local (dashed line). (a) Linear scale of energy. (b) Logarithmic scale of energy with energy measured in keV.

r_s) the calculated surface-plasmon excitation probability (when low-energy protons are used as probe particles) as a function of the kinetic energy E (in keV) of the incident protons. For the purpose of comparison, we have shown the regular hydrodynamical result ($\beta^2 = v_F^2/3$), the simple local result ($\beta = 0$) given by Eq. (9), and a plasmon-pole theoretic[11] result where β^2 is chosen to be a function of wave vector q which reduces to the regular hydrodynamical result in the long-wavelength limit ($q \rightarrow 0$). The particular form for β is chosen according to the prescription suggested[11] by Lundqvist, and by Overhauser in the context of bulk self-energy calculation due to electron-electron interaction. We take,

$$\beta^2(q) \equiv \left[\frac{v_F^2}{3}\right]\left[\frac{1}{2} + \left[\frac{1 - q^2/4k_F^2}{z/k_F}\right] \times \ln\left|\frac{1+q/2k_F}{1-q/2k_F}\right|\right]^{-1} . \tag{11}$$

For this form of the electronic compressibility, the hydro-

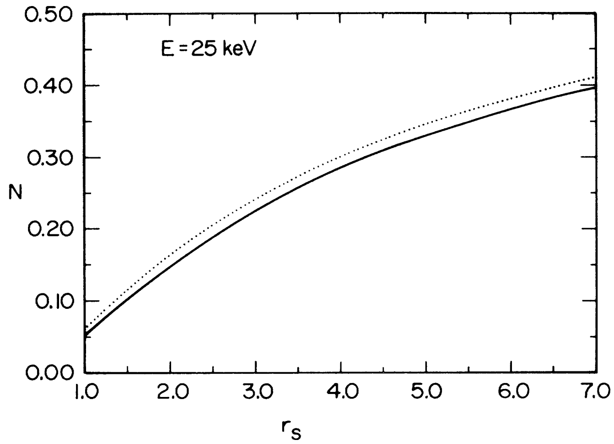

FIG. 3. Shows the dependence of the average number of surface-plasmon excitations as a function of the metallic r_s value for a fixed energy (25 keV) of the external proton. The solid and dotted curves are, respectively, the plasmon-pole and hydrodynamical approximation. The corresponding local result is a constant of about 0.75.

dynamic theory becomes an effective plasmon-pole theory, and it incorporates in a crude fashion the contribution due to electron-hole pair excitations. However, in view of the crudeness of the model, this estimate of the surface effects due to electron-hole pair excitations should not be taken too seriously, since electron-hole pair effects would be strongly affected by the use of a more realistic model of the surface, which lets the electrons spill into the vacuum. Thus the rather small difference between the solid (plasmon-pole) and the dotted (hydrodynamic) curves in Fig. 2 can be attributed to electron-hole pair excitation effects. The simple local theory (dashed curve) gives much higher values of excitation probability except at very high energies where all three curves converge asymptotically.

Finally, in Fig. 3 we show the surface-plasmon excitation probability as a function of the r_s parameter for a fixed value ($E=25$ keV) of the energy of the external proton. Results for both the plasmon-pole (solid curve) and the hydrodynamic (dotted curve) are shown. The corresponding local result is a constant (for fixed E) independent of the metallic r_s value and, for $E=25$ keV, is given by $N\approx 0.75$ which is the asymptotic nonlocal result for $r_a \rightarrow \infty$. Clearly for metallic densities ($r_s \sim 3-5$), the surface-plasmon excitation probability is significantly reduced (by factor of 3) by nonlocal corrections for external proton energies around 25 keV.

In a fast-electron energy-loss experiment (which can directly measure the number N calculated in this paper) nonlocal corrections are unimportant since $v \gg v_F$ for fast electrons with kinetic energy in the keV range. As one can see from Fig. 1, nonlocal effects show up only when the velocity of the external probe is comparable to the metallic Fermi velocity. If the external probe is a slow ($\sim$ eV) electron with $v \sim v_F$, then recoil effects (which I neglect) will also be important in the same range where nonlocal corrections are significant. On the other hand, for heavier probe particles (which have much higher kinetic energy in the same velocity range) recoil effects are negligible and calculated nonlocal corrections become significant as shown in Figs. 2 and 3. I would like to point out that the suppression of the infrared divergence in N arising in a local theory that is being discussed in this paper is a direct result of the introduction of a new velocity scale $\beta(\sim v_F)$ in the nonlocal theory. To emphasize this point, I have also calculated the surface-plasmon excitation probability N in a *local* theory by taking into account a finite broadening Γ of the electron gas (such a finite Γ could arise, for example, from impurity scattering effect and is related to the transport relaxation time τ by $\Gamma=\hbar/2\tau$). The calculation is identical to the prescription given above, except that one retains a damping term in the Euler's equation. The calculation is straightforward and the tedious algebra is not shown here. One gets in the local theory ($\beta=0$, $\Gamma\neq 0$):

$$N=\frac{\pi}{2v}[1-O(\Gamma/\omega_s)+\cdots], \tag{12}$$

where the ellipsis represents higher-order corrections in Γ/ω_s, $\omega_s\equiv\omega_p/\sqrt{2}$ is the long-wavelength surface plasma frequency, and $\Gamma \ll \omega_s$ is the finite broadening. This result (which is valid for small Γ) clearly shows that $N(v\rightarrow 0)$ goes as $O(1/v)$ even when $\Gamma\neq 0$ in the local theory. The main effect of having $\Gamma\neq 0$ is to quantitatively reduce N without changing its velocity dependence. Thus, having a nonzero Γ (unlike having $\beta\neq 0$) does not remove the infrared singularity in the calculated surface-plasmon excitation probability (even though it does reduce the total number of surface plasmons excited for a particular value of v). This is not surprising since making $\Gamma\neq 0$ introduces a new energy scale in the problem (originally one had only ω_s) but no new velocity scale. Incorporating nonlocal effects, however, introduces a new velocity scale $\beta(\sim v_F)$ which saturates the effect of the external velocity v when $v \lesssim v_F$ and removes the unphysical infrared divergence.

Before concluding, we want to emphasize that in this paper the average number of *real* surface plasmons excited by the external charge has been calculated in a nonlocal theory. This is different from the corresponding calculation for *virtual* excitations which are also created during the interaction between the external charge and the surface. These virtual excitations are, in fact, related to the conservative part of the work done by the external charge which vanishes when the probe particle goes back to its original starting position at infinity. Thus, there are no virtual excitations left in the system. However, the real excitations calculated in this paper are related to the dissipative work done by the external probe and can be detected in an experiment (such as, fast-electron energy-loss experiment). It is well known that the number of virtual excitations is related directly to the image-potential energy which vanishes when the probe particle is infinite distance away. In some recent publications[12] there is some confusion about this issue and, in fact, some of these papers[12] actually calculate the average number of virtual excitations created by the external probe which, as I have emphasized, is not an experimentally relevant quantity.

In summary, I have calculated the average number of *real* plasmons created by an external charged particle in its interaction with a metal surface by using hydrodynamic (and, plasmon-pole) response formalism. The infrared divergence inherent in local theories is suppressed by nonlocal corrections, and the excitation probability goes to zero as the velocity of the probe particle vanishes (whereas in a local theory it diverges as v^{-1}). I show that for low-energy external protons ($\lesssim 25$ keV) interacting with the metal surface, nonlocal effects are quantitatively very significant and reduce the excitation probability by about a factor of 3 compared with the local theory.

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