Sensitivity of Surface-Plasmon Dispersion and Damping to Potential Barrier Shape

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I have evaluated exactly the random-phase-approximation surface-plasmon linear dispersion coefficient,

$$\alpha=\alpha_1+i\alpha_2\equiv\lim_{q\to 0} q^{-1}[\omega_s(q)/\omega_s(0)-1],$$

for $2\leq r_s\leq 6$, using self-consistent (Lang-Kohn) potential barriers, and also using model barriers of adjustable surface diffuseness, a. I find α to be markedly sensitive to a, casting doubt on the reliability of using non-self-consistent model barriers to determine surface-plasmon properties. At Al density ($r_s\simeq 2$), for example, I find $\alpha=-(0.24+0.57i)$ Å using the Lang-Kohn potential, in contrast to Beck and Celli's step-function ($a=0$) barrier result, $\alpha=-(0.07+0.2i)$ Å.

Because the excitation of surface plasmons plays an important role in mediating the interaction between a fast charged particle and a metal surface,[1] considerable effort has been expanded in attempting to solve microscopic models of surface-plasmon properties,[2-6] this despite the substantial mathematical difficulties involved. Such theoretical work has recently assumed greater importance, with the publication of the first measurements of surface-plasmon dispersion and damping for a characterized surface [Al(111)].[7]

It is only within the last year that any microscopic results have been reported for a model in which the surface potential barrier corresponds to a finite ($<\infty$) work function, and these results[2] were based on a new variational method[2,8] whose accuracy has, until now, not been tested.

In this Letter, I report the first exact random-phase-approximation (RPA) calculations of surface-plasmon properties, for model surfaces characterized by smooth, finite potential barriers. I have obtained results for the self-consistent barriers of Lang and Kohn,[9] as well as for model barriers of adjustable surface diffuseness, a, and work function, Φ. These results, for conduction-electron densities corresponding to electron gas radii r_s between 2 and 6, are presented in Figs. 1 and 2.

I find that the parameters of the surface dispersion relation depend sensitively on the shape of the assumed potential barrier. For example, the linear coefficients of surface-plasmon dispersion and damping, for the asymmetric (i.e., mostly concave downwards) Lang-Kohn barriers, are systematically only about $\frac{1}{2}$ as large as they are for symmetric model barriers of comparable surface diffuseness. This result is illustrated in Fig. 1. I also find that the linear coefficients for the Lang-Kohn barrier at Al density ($r_s\simeq 2$) have values about 3 times as large in magnitude as those reported by Beck and Celli[2] for a step-function barrier. In Fig. 2, this discrepancy is put in perspective, as the linear coefficients are shown to be quite rapidly varying functions of barrier diffuseness.

The linear coefficients α_1 and α_2 are defined

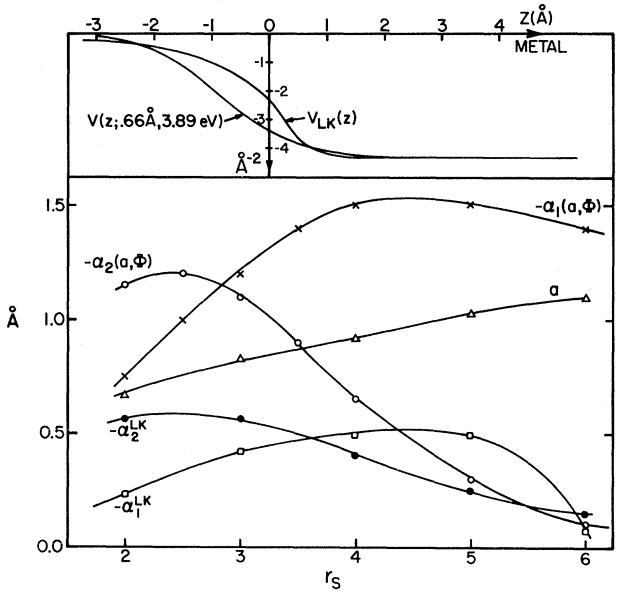

FIG. 1. Dependence of α_1 and α_2 on r_s. The curves labeled $-\alpha_1{}^{LK}$ and $-\alpha_2{}^{LK}$ were calculated using the Lang-Kohn potential. The curves labeled $-\alpha_1(a,\Phi)$ and $-\alpha_2(a,\Phi)$ were calculated using $V(z;a,\Phi)$, with the values of a that are shown, and values of Φ taken from Ref. 9. Inset, comparison, for $r_s=2$, in units of Å^{-2}, of $(2m/\hbar^2)V_{LK}(z)$ and $(2m/\hbar^2)V(z;0.66\text{ Å},3.89\text{ eV})$.

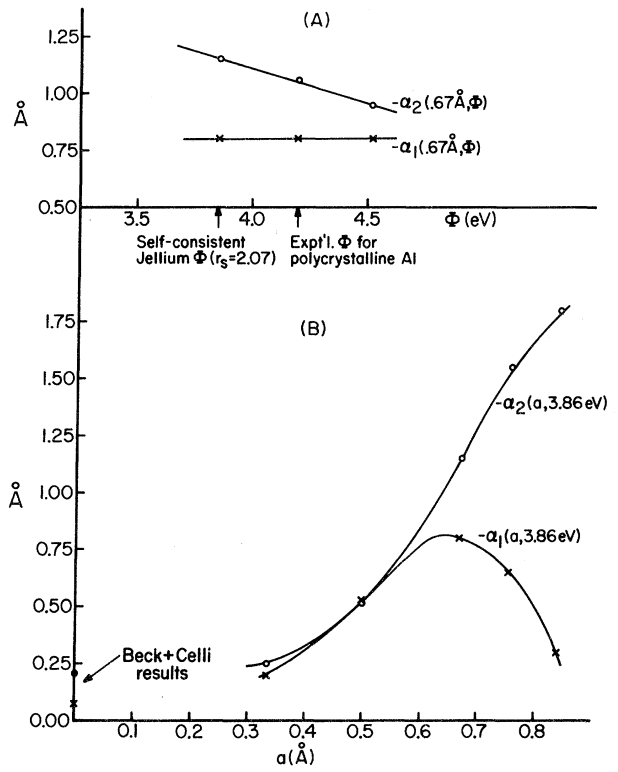

FIG. 2. (a) Dependence of $\alpha_1(0.67\ \text{Å}, \Phi)$ and $\alpha_2(0.67\ \text{Å}, \Phi)$ on Φ, for $r_s=2.07$. (b) Dependence of $\alpha_1(a, 3.86\ \text{eV})$ and $\alpha_2(a, 3.86\ \text{eV})$ on a, for $r_s=2.07$. Beck and Celli's variational $a=0$ results (Ref. 2) are also shown.

in terms of the small-wave-vector expansion of $\omega_s(q)$, the (complex) surface-plasmon frequency[10]:

$$\omega_s(q)=\omega_s(0)[1+(\alpha_1+i\alpha_2)q+O(q^2)]. \quad (1)$$

The curves in Fig. 1 labeled $-\alpha_1{}^{LK}$ and $-\alpha_2{}^{LK}$ were calculated using Lang-Kohn potentials, while those labeled $-\alpha_1(a, \Phi)$ and $-\alpha_2(a, \Phi)$ were calculated using model barriers of the form

$$V(z; a, \Phi) = -(\epsilon_F+\Phi)[1+\exp(z/a+bz^3/a^3)]^{-1}. \quad (2)$$

In Eq. (2), z is the coordinate normal to the surface plane, while ϵ_F, Φ, and a are, respectively, the Fermi energy, work function, and surface diffuseness parameter corresponding to whatever the value of r_s. The z^3 term in $V(z; a, \Phi)$ was introduced for the sake of computational convenience; by choosing $b=\frac{1}{125}$, I ensured that this term would not affect my quantitative results appreciably.

The curves of Fig. 1 were calculated using values of Φ obtained self-consistently by Lang and Kohn before "lattice corrections,"[9] and using values of a chosen by requiring $V(z; a, \Phi)$ to equal $V_{LK}(z)$, the Lang-Kohn potential, at the two points where its value are $10\%\times(\epsilon_F+\Phi)$ and $90\%\times(\epsilon_F+\Phi)$ below the vacuum level. These values of a are shown in Fig. 1. The inset is a comparison of the Lang-Kohn barrier and $V(z; 0.66\ \text{Å}, 3.89\ \text{eV})$, for $r_s=2$.

It is worth noting in Fig. 1, finally, that in general α_1 is negative, despite the strong sensitivity of the α's to barrier shape. It was the observation of negative values of α_1, by keV electron transmission on uncharacterized Mg ($r_s=2.67$) surfaces,[11] and later by inelastic low-energy electron diffraction on an Al(111) surface,[7] that provoked much of the recent work on surface-plasmon properties. Bennett[12] first showed the unexpected sign of α_1 to be understandable in the context of a hydrodynamic model of the electron fluid surface. His results were corroborated in the variational RPA calculation of Beck and Celli,[2] and are corroborated again here in exact RPA calculations for a variety of potential barrier shapes.

In Fig. 2, for Al density ($r_s=2.07$), I exhibit the dependence of the α's on Φ and a, the work function and surface diffuseness parameters of the model potential barrier of Eq. (2). In Fig. 2(a), it is seen that the dependence of the α's on Φ is rather weak, at least on the scale of difference in Φ that one might expect from crystal anisotropy. In Fig. 2(b), however, it is shown that the variation of the α's with a is remarkably rapid. The values of α_1 and α_2 decrease in magnitude by factors of ~4 and ~5, respectively, between the values of $a=0.67$ Å, for which $V(z;$ 0.67 Å, 3.86 eV) and $V_{LK}(z)$ are of comparable diffuseness (cf. inset of Fig. 2), and $a=0.335$ Å, which is $\frac{1}{2}$ this approximately self-consistent diffuseness. The trend of the α's, as a decreases, does seem to be in the direction of the Beck and Celli step-function ($a=0$) barrier variational results,[2] lending credence to the reliability of the variational method. However, the rapid variation of the α's with a also forces one to conclude that the agreement of the zero-diffuseness dispersion coefficient and that observed experimentally[7] is accidental. This latter conclusion is supported by the fact that in recent improved experiments,[13] the dispersion coefficient for Al(111) appears to have changed in sign and increased in magnitude by a factor of ~3.

The method I used to put the RPA equation into

a form suitable for numerical involves a combination of the manipulations previously used[10] to solve it generally at $q=0$, and the partial separation method used by Beck in his infinite-wall–model work.[3] The form of the RPA equation which is most convenient for expansion in powers of q [cf. Eq. (1) of the second paper of Ref. 5] is

$$\varphi_{q\omega}(z)=\frac{2\pi e^2}{m\omega}\int\frac{d^2k}{(2\pi)^2}\int_0^\infty\frac{2\,d\kappa}{\pi}2\theta_{k\kappa}\int dz''\,dz'\left\{\exp(-q|z-z'|)\left[\vec{k}\cdot\hat{q}\psi_\kappa(z')-\mathrm{sgn}(z-z')\frac{d\psi_\kappa}{dz'}+\psi_\kappa(z)\,\delta(z-z')\right]\right.$$
$$\left.\times\,\mathcal{G}_{k,q,\omega}^{-}(z',z'')\right\}\psi_\kappa(z'')\varphi_{q\omega}(z''). \quad (3)$$

In Eq. (3), the unknown function $\varphi_{q\omega}(z)$ is the electrostatic potential fluctuation associated with a surface plasmon of frequency $\omega\equiv\omega_s(q)$. The wave function $\psi_\kappa(z)$ is the solution of energy ω_κ to the one-dimensional Schrödinger equation with $V(z)$ as the potential, and the symbol $2\theta_{k\kappa}$ represents the zero-temperature Fermi function, $2\theta(\epsilon_F-k^2/2m-\omega_\kappa)$. Finally the function $\mathcal{G}_{k,q,\omega}^{-}(z,z')$ represents the difference between the outgoing and ingoing one-dimensional Green's functions corresponding to $V(z)$, evaluated at energies $\omega_\kappa+[k^2-(\vec{k}+\vec{q})^2]/2m+\omega$ and $\omega_\kappa+[k^2-(\vec{k}+\vec{q})^2]/2m]-\omega$, respectively, and at depths z and z'. The first step in reducing Eq. (3) to manageable form is the extraction of the $q=0$ solution, namely $\omega_s(0)=\omega_s=\omega_p/\sqrt{2}$ and $\varphi_{0\omega}=\mathrm{const}=1$, which holds[10] whatever the form of $V(z)$. I accomplish this by defining the "fluctuating surface charge" $\sigma_{q\omega}$ as

$$\sigma_{q\omega}\equiv-\frac{2\pi e^2}{m\omega}\int\frac{d^2k}{(2\pi)^2}\int_0^\infty\frac{2\,d\kappa}{\pi}2\theta_{k\kappa}\int dz'\,dz''\frac{d\psi_\kappa}{dz'}\mathcal{G}_{kq\omega}^{-}(z',z'')\psi_\kappa(z'')\varphi_{q\omega}(z'), \quad (4)$$

and by defining a new unknown function $\nu_{q\omega}(z)$ according to

$$\nu_{q\omega}(z)\equiv(1-\omega_p^2/\omega^2)\varphi_{q\omega}(z)-\sigma_{q\omega}. \quad (5)$$

Equation (5) is to be substituted into Eq. (3) yielding an inhomogeneous equation for $\nu_{q\omega}(z)/\sigma_{q\omega}$. The requirement that the $\nu_{q\omega}(z)/\sigma_{q\omega}$ which satisfies this equation must also satisfy Eq. (4) yields the surface-plasmon frequency $\omega_s(q)$.[14] At $q=0$, it is easy to verify that $\sigma_{0\omega}=-\omega_s^2/\omega^2$ and therefore that $\nu_{0\omega}(z)=0$. Thus $\nu_{q\omega}(z)$ is a quantity of $O(q)$ compared to $\varphi_{q\omega}$.[15]

The assumption that ω can be expanded in powers of q is equivalent to the assumption that, in solving for $\nu_{q\omega}(z)/\sigma_{q\omega}$, contributions to z integrals from regions of the z axis far from the surface are negligible. In this case the equation for $\bar{\nu}_{q\omega}(z)\equiv\nu_{q\omega}(z)/\sigma_{q\omega}$ assumes the small-q form

$$\bar{\nu}_{q\omega}(z)=\frac{q}{n_\infty}\int_{-\infty}^{\infty}dz'\,(z-z')\frac{dn_0}{dz'}+\frac{\omega_s}{n_\infty}\int\frac{d^2k}{(2\pi)^2}\int_0^\infty\frac{2\,d\kappa}{\pi}2\theta_{k\kappa}\int dz'\,dz''\left[2\theta(z'-z)\frac{d\psi_\kappa}{dz'}+\delta(z'-z)\psi_\kappa(z')\right]$$
$$\times\,\mathcal{G}_{k,0,\omega_s}^{-}(z',z'')\psi_\kappa(z'')\bar{\nu}_{q\omega}(z''), \quad (6)$$

where $n_0(z)$ is the electron density profile, and where $n_\infty\equiv n_0(\infty)$.

Equation (6) has one serious disadvantage, namely, that its inhomogeneous term diverges linearly as $z\to\infty$. It can easily be shown by iteration that this divergence is not serious enough to violate the condition which permits the q expansion. Nevertheless, such a divergence would be troublesome numerically, and therefore I have carried out one further redefinition of the unknown function, letting[16]

$$\Delta_{q\omega}(z)\equiv\frac{1}{q}\bar{\nu}_{q\omega}(z)+z-\frac{1}{n_\infty}\int dz'\,z'\frac{dn_0}{dz'}-\frac{1}{m\omega^2}\frac{dV}{dz}. \quad (7)$$

The function $\Delta_{q\omega}(z)$ can be shown to behave asymptotically deep inside the metal as a sum of six (or eight[17]) oscillating exponentials times z^{-2}, i.e., it dies off with Friedel-like oscillations. Outside the metal, as $z\to-\infty$, $\Delta_{q\omega}(z)$ still diverges linearly, but in this region the divergence presents no problem, because in all of the necessary z integrations $\Delta_{q\omega}(z)$ is multiplied by one or more wave functions which die off exponentially there. I make use of my explicit knowledge of the asymptotic form of $\Delta_{q\omega}(z)$ to reduce the integral equation for it to an equation which essentially covers only a compact domain of z axis about the jellium surface. Such an integral equation can be straightforwardly solved to arbitrary

accuracy by matrix inversion, using a sufficiently fine numerical integration mesh. Because of the crudeness of the surface model that I have used, i.e., one that neglects departures from two-dimensional translational invariance, I have not attempted to solve for $\Delta_{q\omega}(z)$ and $d\omega/dq|_{q=0}$ to better than about ± 5% accuracy.

The introduction of departures from surface flatness (specularity), if only those due to lattice periodicity, will certainly be the next significant step in the development of the theory of surface plasmons. The most recent Al(111) data, for example, cannot be explained without assuming that $\mathrm{Im}\omega_s(0)/\mathrm{Re}\omega_s(0) = 18\%$, which is a good indication that departures from two-dimensional translational invariance are important.[10] Presumably the way to take account of lattice periodicity or surface-roughness effects is by perturbative methods applied to flat-surface models; such methods, moreover, will be more likely to converge if the unperturbed model surface potential barrier is smooth and finite (as well as self-consistent), than if it is discontinuous. Thus the present calculations should provide a basis for progress toward a more realistic evaluation of surface-plasmon properties.

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[10]Independent of the shape of the potential barrier, for a flat surface and within the RPA, $\omega_s(0)=\omega_p/\sqrt{2}$, where ω_p is the classical plasma frequency. This is proven in the second paper of Ref. 5.

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[14]In passing, it should be noted that the formula I obtain for $\omega_s(q)$ turns out to be formally identical to that derived, but never applied, by J. Harris and A. Griffin, Phys. Lett. 34A, 51 (1971), Eq. (5).

[15]Since $\nu_{q\omega}$ is of $O(q)$ it contains, *in leading order*, information concerning surface plasmon properties which are linear in q. Were I to solve the RPA directly for $Q_{q\omega}(z)$, I would have to subtract $\varphi_{0\omega}(z)$ from it to obtain this information. Since subtracting large numbers to obtain small answers is a numerical process which introduces large errors, it is essential to perform the subtraction exactly. This exact subtraction is precisely what is accomplished by introducing the quantities $\nu_{q\omega}(z)$ and $\sigma_{q\omega}$ in Eqs. (4) and (5).

[16]The introduction of the term $-(1/m\omega^2)\,dV/dz$ into the definition of $\Delta_{q\omega}(z)$ turns out to be convenient. Its introduction is not necessary in order to cure the divergence difficulty associated with Eq. (6). It should be noted that the signs of the second and third terms on the right-hand side of Eq. (6) are correct as they stand.

[17]Depending on whether $\epsilon_F < \omega_s(0)$ or $\epsilon_F > \omega_s(0)$.