Charge renormalization describing plasmon dispersion in metals

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We derive a plasmon dispersion relation to describe the measurements of electron-energy-loss spectroscopy. We replace the random-phase-approximation (RPA) theory with a new, zeroth-order theory that matches measurements better than the RPA theory. In our new theory, electrons are trapped in a lattice wave; this trapping lowers the electron momentum and increases the electron interaction energy with the wave.

I. INTRODUCTION

It is generally agreed[1-5] that currently available theories do not satisfactorily explain plasmon dispersion measurements of electron-energy-loss spectroscopy (ELS). Current theories, which yield the plasmon dispersion relation, are based on a zeroth-order, random-phase-approximation (RPA) theory derived in Ref. 6, and even though calculations have been made of higher-order corrections to the RPA, exchange and correlation effects,[7,8] and the effect of lattice polarization,[2] these corrections do not lead to a theory that is entirely satisfactory.

The Vashishta-Singwi (VS) (Ref. 7) theory uses local-field corrections to calculate the exchange and correlation energy. The VS theory is an electron-electron interaction theory which goes beyond the RPA, and there are other theories of this type: The correlation energy has been calculated for a two-dimensional (2D) metal using the Hubbard approximation and VS theory.[8] The correlation energy has been calculated for 2D and quasi-2D metal using a coupled-cluster approximation,[9] and the correlation energy has been calculated in the 2D ladder approximation.[10] The effect of finite thickness of the 2D metal on correlation energy has been considered,[11] the lowest subband has been modeled as a potential well, and the effect on correlation energy of confining an electron to the potential well has been calculated.[12] These theories are electron-electron interaction theories; the correctness of these theories is usually determined by comparison among themselves or to a set of rules generally accepted as correct.[13] Theoretical results have not been compared to experimental results, and direct comparison of these theories to ELS data is not possible since ELS data show dependence on the lattice.[1,2] However, with the trapping theory developed here, it may be possible for the first time to compare electron-electron interaction theory to experiment by using the trapping theory as zeroth order and using the electron-electron interaction theory to explain the remaining discrepancies.

Sturm[1,2] alone includes the effect of the lattice; he calculates the effect of an electron inside a lattice potential well; he considers the lattice potential to be a higher-order correction to the RPA. His results do not fit measurements; this lack of agreement with experimental may be the result of using the RPA.

The trapping theory we develop has lattice dependence since we trap electrons in a lattice wave. The lattice effect is zeroth order and leads to a zeroth-order theory which replaces the RPA. Comparison of our theory with the measurements made on several different experiments on several different metals shows that our explanation of electron energy loss due to electron trapping is more correct than the RPA theory.

We confine our attention to small momentum transfer; in this case, the plasmon frequency equals the electron plasma frequency plus a correction quadratic in transferred momentum; the correction coefficient is α. RPA theory derives an $\alpha_{\rm RPA}=3\epsilon_F/(5\omega_p)$, where ϵ_F is the Fermi energy and ω_p is the electron plasma frequency. We will use renormalization to replace the RPA theory with a new theory in which an electron is "trapped" in a lattice wave, in analogy with electron trapping in high-temperature plasma waves.[14] The lattice wave is classical; the electron is a quantum particle in a stable state with momentum lower than the Fermi momentum and large interaction energy from interactions with the lattice wave. From the electron trapping assumption, we derive a theory that predicts an antilinear dependence of α on k_D^2/ω_p. k_D is the Debye wave number. We will show that the measured correction coefficients α_m show antilinear dependence on k_D^2/ω_p, as predicted by the trapped-electron theory.

II. ELECTRON TRAPPING AND ELECTRON PROPAGATOR

Classical plasma theory describes a resonance condition called trapping in which electron velocity p/m equals wave phase velocity ω/k[14]:

$$\omega-\mathbf{k}\cdot\mathbf{p}/m=0\ . \tag{1}$$

$\mathbf{p}$ is electron momentum, m is electron mass, ω is wave energy, and $\mathbf{k}$ is wave momentum. This condition is called trapping, since an electron is trapped in the trough of the wave. In the trapped condition, the electron maintains a constant phase with respect to the wave; in the trough, the wave amplitude is a minimum; hence, the

electron experiences the large and constant electric field of the wave.

We assume that there is a quantum analog to classical trapping; an electron is quantumly trapped when it meets three conditions: condition (a), the electron momentum $\mathbf{p}$ satisfies condition (1) for some wave with frequency ω and wave number $\mathbf{k}$; condition (b), the electron forms a stable state, a state with a long lifetime, and condition (c), the electron has a large interaction energy from interaction with the wave, and this energy is large enough for the electron to form an allowed state.

In our case we assume that the electron is trapped in a lattice wave; the frequency in condition (1) is the Debye frequency ω_D and the wave number is the Debye wave number $\mathbf{k}_D$. We write the momentum of the trapped electron as $\mathbf{p}=\mathbf{p}_F-\mathbf{k}$; $\mathbf{p}_F$ is the Fermi momentum and $\mathbf{k}$ is the momentum of the wave absorbed by the electron. We assume that $\mathbf{p}$ satisfies condition (1). We take $\mathbf{k}$ as positive and note that the total momentum of an electron is smaller than the Fermi momentum. We write the energy of a trapped electron $\epsilon=\epsilon_F+\omega$ where ϵ_F is the Fermi energy, ω is positive, and $\epsilon-p^2/(2m)$ is the energy of an electron due to its interaction with the wave. For the set of metals we consider (Sb Sn In Ga Al Mg K Be Li Na), the ratio of lattice-wave phase velocity, velocity of sound, to the metal's Fermi velocity varies from 0.03 to 0.09. Since these ratios are much smaller than 1, the kinetic energy $p^2/(2m)$ is much smaller than the Fermi energy for each metal. We will find that the contribution to plasmon energy from the α_{RPA} term is proportional to the kinetic energy, and since this energy is small, the plasmon energy has little dependence on the α_{RPA} term.

To guide us in forming our trapping model, we first consider the Hamiltonian for an electron-phonon interaction; in the spatial representation, $H'_{e-n}=\gamma\hat{\psi}^{\dagger}\hat{\psi}\hat{\phi}$.[15] $\hat{\psi}$ ($\hat{\phi}$) is the electron (phonon) field operator. We let $\mathbf{u}$ be the phase velocity of a phonon with energy ω and momentum $\mathbf{k}$; $u=\omega/k$. We transform into the frame of the phonon, using $\mathbf{x}=\mathbf{x}'+\mathbf{u}t$. The phonon field operator which is proportional to $e^{-i(\omega t-\mathbf{k}\cdot\mathbf{x})}$ is transformed into $\phi\sim e^{-i(\omega-\mathbf{k}\cdot\mathbf{u})t}e^{i\mathbf{k}\cdot\mathbf{x}'}$. If we vary the velocity $\mathbf{u}$ or the position $\mathbf{x}'$, we see that the H'_{e-n} energy varies sinusoidally. The idea of trapping is that the electron with velocity $\mathbf{u}$ is trapped in a single trough of a wave and stays in the trough. We can form this model if $\phi\sim e^{-|\omega-\mathbf{k}\cdot\mathbf{u}|t}e^{\mathbf{k}\cdot\mathbf{x}'}$, and $\mathbf{x}'\to 0$. Transforming back to the unprimed frame, $\phi\sim e^{-\omega t+\mathbf{k}\cdot\mathbf{x}}$, and we carry the condition that the quantity $\omega-\mathbf{k}\cdot\mathbf{u}$ is positive. We let H_{e-n} be the electron-phonon interaction energy of a trapped electron. Since $H_{e-n}\sim e^{-\omega t+\mathbf{k}\cdot\mathbf{x}}$, we see that our electron is trapped in a potential well with exponential sides.

Renormalizing using H_{e-n} leads, in general, to an electron mass and charge correction; we look at the simplest form of renormalization. Electron trapping is analogous to putting an electron into a potential well. If the potential well has a finite depth, γ finite, we would obtain mass and charge corrections that vanish with γ. On the other hand, if we take γ infinite, we confine the electron strictly to the potential well; the γ terms are neglected. (In the best tradition of renormalization theory, we have neglected an infinite term.) Just as it does in the potential-well problem, we find that this approach leads to sensible results.

We now transform from the spatial representation to the momentum representation; in so doing, we obtain the conservation of momentum and energy relations at the vertex. We can represent the trapped electron with the modified-Hartree-Fock diagram shown in Fig. 1(a). the effect of electron trapping is to change the electron energy and momentum; it is convenient to write the energy of a trapped electron

$$\Upsilon=\epsilon+i\omega_i \tag{2}$$

and its momentum

$$\mathbf{P}=\mathbf{p}+i\mathbf{k}_i\ . \tag{3}$$

$\mathbf{k}_i$ and ω_i are the wave number and frequency of the lattice wave, and we should keep in mind that $\omega_i-\mathbf{p}\cdot\mathbf{k}_i/m$ is positive.

Using (2) and (3) for the total energy and momentum along with Ref. 15, we write the propagator for the trapped electron as

$$G^0=\frac{1}{\Upsilon-P^2/(2m)}$$
$$=\frac{1}{\epsilon-p^2/(2m)+k_i^2/(2m)-i|\omega_i-\mathbf{p}\cdot\mathbf{k}_i/m|}\ . \tag{4}$$

The propagator in (4) has a pole which defines a quasiparticle; the lifetime of this quasiparticle is $\tau=0.5|\omega_D-\mathbf{p}\cdot\mathbf{k}_D/m|^{-1}$. The trapping of an electron in a potential well has led to a renormalization of the electron with a self-energy $\Sigma=i|\omega_i-\mathbf{p}\cdot\mathbf{k}_i/m|$. We see that condition b for a trapped electron is satisfied when condition a is satisfied.

III. POLARIZATION AND DISPERSION RELATION

We calculate the polarization of the metal by renormalizing the Coulomb interaction between electrons. We use G^0, renormalized by electron trapping, as the basis for renormalization of the electron-electron interactions.

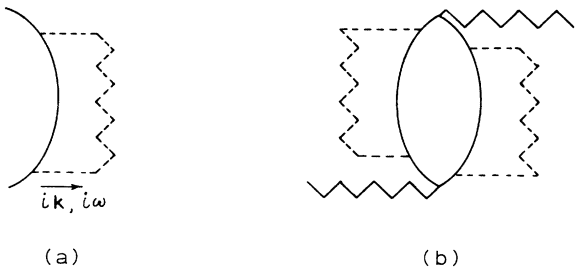

FIG. 1. (a) Propagator for trapped electron. Solid line is an electron propagator; dashed line is a phonon propagator. (b) Ring diagram of trapped electron and hole. Solid, wavy line is a Coulomb interaction.

We renormalize by finding the contribution to polarization from ring diagrams.[15] A ring is formed by an electron inside the Fermi sphere absorbing a plasmon to form an electron-hole pair. In the new theory presented here, both the electron and the hole, of the electron-hole pair, become trapped. The modified, ring diagram depicting this trapping is shown in Fig. 1(b). Using (4), we write the polarization

$$\Pi=\tfrac{1}{2}\int_0^\infty d\epsilon\int_{-\infty}^{\infty}d\omega\int_{-\infty}^{\infty}d\mathbf{p}\int_{-\infty}^{\infty}d\mathbf{k}\,f_\epsilon f_\omega f_{\mathbf{k}}(f_{\mathbf{p}}-f_{\mathbf{p}-\mathbf{k}'})\left[\frac{1}{\Upsilon-P^2/(2m)}\frac{1}{\Upsilon^*+\omega'-(\mathbf{P}^*+\mathbf{k}')^2/(2m)}+\text{c.c.}\right]. \tag{5}$$

c.c. is the complex conjugate of the first term. f_ϵ, f_ω, $f_{\mathbf{k}}$, and $f_{\mathbf{p}}$ are probability densities; they are non-negative and normalized to unity. $f_{\mathbf{p}}$ is the probability that an electron has momentum $\mathbf{p}$; f_ϵ is the probability that the electron has energy ϵ, and so on, for f_ω and $f_{\mathbf{k}}$.

We assume that $f_k\sim\delta(\theta_k)+\delta(\theta_k-\pi)$ where θ_k is the angle between $\mathbf{k}$ and $\mathbf{k}'$, and we use the sifting property of the δ function. We take $f_\omega=1/(2\pi)$, and integrate over ω, using the poles at $i((\mathbf{P}^*+\mathbf{k}')^2/(2m)-\epsilon-\omega')$ and $i(P^{*2}/(2m)-\epsilon)$, and we integrate over ϵ using $f_\epsilon=\delta(\epsilon-(p^2-k^2)/(2m))$ to find

$$\Pi=\frac{-1}{2}\int_{-\infty}^{\infty}d\mathbf{p}\int_{-\infty}^{\infty}d\mathbf{k}\,f_{\mathbf{k}}(f_{\mathbf{p}}-f_{\mathbf{p}-\mathbf{k}'})\left[\frac{1}{\omega'-\mathbf{P}\cdot\mathbf{k}'/m-k'^2/(2m)}+\text{c.c.}\right]. \tag{6}$$

If $k=0$ and k'/p is small, (6) is the polarization of Ref. 16. We take $f_{\mathbf{k}}=\delta(k-k_D)/(4\pi k_D^2)$ and integrate over $\mathbf{k}$; we take $f_{\mathbf{p}}=f_p/(4\pi)$ and integrate over the angles of momentum $\mathbf{p}$. We expand the denominator of (6) in small $(pk'/\omega'\ kk'/\omega'\ k'^2/\omega')$ to find

$$\Pi=\frac{-k'}{m\omega'^2}\int_0^\infty dp(f_p-f_{p-k'})\left[\frac{p^3}{3}+\frac{p^3}{3}\frac{k'^2}{m\omega'}+\frac{p^5k'^2}{5m^2\omega'^2}-\frac{p^3k'^2k_D^2}{3m^2\omega'^2}+\frac{p^3k'^4}{4m^2\omega'^2}\right]. \tag{7}$$

In the integrand of (7), we take k'/p small and write $(f_p-f_{p-k'})=\mathbf{k}'\cdot\partial f_p/\partial\mathbf{p}$; we then integrate by parts. In the integrals containing p^3, we use the normalization of f_p; from the integral containing p^5, we define $\varepsilon=(1/2m)\int dp\,p^4f_p$. ε is the kinetic energy of electrons excited from the Fermi sphere; ε is typically the Fermi energy, and using the Fermi energy, the third term in (7) yields the α_{RPA}. For a trapped electron, however, ε may be much smaller than the Fermi energy.

Once we have the polarization, we use Dyson's equation to calculate the dielectric constant[15]; then setting the dielectric constant to zero, we find for the small $k'^2/(m\omega_p)$ expansion of the plasmon dispersion relation

$$\omega\doteq\omega_p+\alpha\frac{k'^2}{m}+\beta\frac{k'^4}{2m^2\omega_p}, \tag{8}$$

where

$$\alpha=\alpha_1+\alpha_2\frac{k_D^2}{2m\omega_p}+\alpha_3\frac{\varepsilon}{\omega_p}. \tag{9}$$

ω_p is electron plasma frequency, and the theoretical values are $\alpha_1=0.5$, $\alpha_2=-1$, $a_3=1$, and $\beta=0.75$.

IV. COMPARISON TO EXPERIMENTAL RESULTS

Reference 1 reports measured values of alpha α_m from experiments conducted by those in Refs. 17 and 18, and we include the measurements of Refs. 4 and 5.

We set $\varepsilon=\epsilon_F$ making the third term of (9) $\alpha_3\alpha_{\text{RPA}}$. Using multiple linear regression, we fit the measured value of α_m, for the set of metals (Li Na Mg Al In Sn Sb), to Eq. (9); we find $\alpha_1=1.54$, $\alpha_2=-1.10$, and $\alpha_3=6\times10^{-4}$. Because α_2 is zeroth order and α_3 is of the order of 10^{-3}, we see that the measured values of α_m fit the Debye-momentum-squared term and not the RPA term in (9). The correlation coefficient[19] between α_m and k_D^2/ω_p is -0.9; the correlation coefficient between α_m and α_{RPA} is 0.6; α_m is more highly correlated with k_D^2/ω_p than with α_{RPA}. From here on we set $\alpha_3\equiv0$, since the data show low correlation between the measured value of α and α_{RPA}.

RPA theory not only does not show correlation with the data, its magnitude is wrong. It is reported that α_{RPA} is roughly twice the measured value,[2] but the error is larger than this when (6) is used to calculate the RPA term. Using (6), the magnitude of α_{RPA} is more than five times the measured value.

In Fig. 2, we plot α_m versus $k_D^2/(2m\omega_p)$ for (Sb Sn In Ga Al Mg K Be Li Na). The dashed line in Fig. 2 is the linear-regression fit to α_m values of (Sb Sn In Al Mg K Li Na); the solution is given by (9) with $\alpha_1=0.57$, $\alpha_2=-0.47$, and $\alpha_3=0$. We see that Sn, In, Mg, and K fall on a straight line, the solid line in Fig. 2; the equation of this line is given by (9) with $\alpha_1=0.79$, $\alpha_2=-0.84$, and $\alpha_3=0$. The slopes of the curves in Fig. 2 are negative, which match the negative slope predicted by the theory; and the negative measured slope confirms the validity of our use of momentum exchange ik_D in the electron momentum $\mathbf{P}$.

Sturm[1] has reevaluated reported values of α_m by looking at the slope of ω versus k'^2 near k' zero. Sturm[1] changed reported values of α_m by as much as a factor of

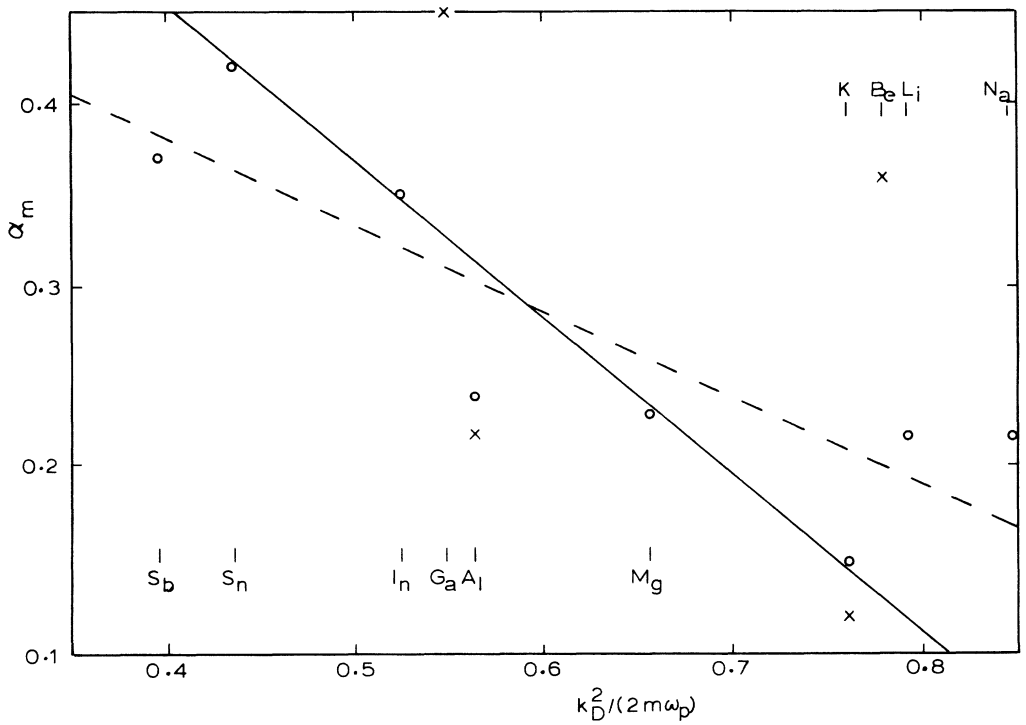

FIG. 2. Plot of measured alpha α_m vs (Debye wave number squared) /(2 m electron plasma frequency), $k_D^2/(2m\omega_p)$, for (Sb Sn In Ga Al Mg K Be Li Na). The solid straight line fits (Sn In Mg K) with $\alpha_m = 0.79 - 0.84 k_D^2/(2m\omega_p)$. The dashed line is a linear-regression fit to (Sb Sn Al Mg K Li Na) yielding $\alpha_m = 0.57 - 0.47 k_D^2/(2m\omega_p)$. Points labeled with × are not included in the determination of parameters.

2. Since α_m can vary greatly with interpretation of data, along with the multiple values reported for α_m (× points for Al and K in Fig. 2 are dual values[1]), there is uncertainty in the measured values of α. If we assume that this uncertainty makes both the dashed line and the solid line an acceptable fit to the data in Fig. 2, then we can say that the measured values of α_1 and α_2 are close to the theoretical values, with errors of 13% and 17%, respectively. We note that three reevaluated values of α_m, for (Sn In Mg), lie on a straight line in Fig. 2. And since the

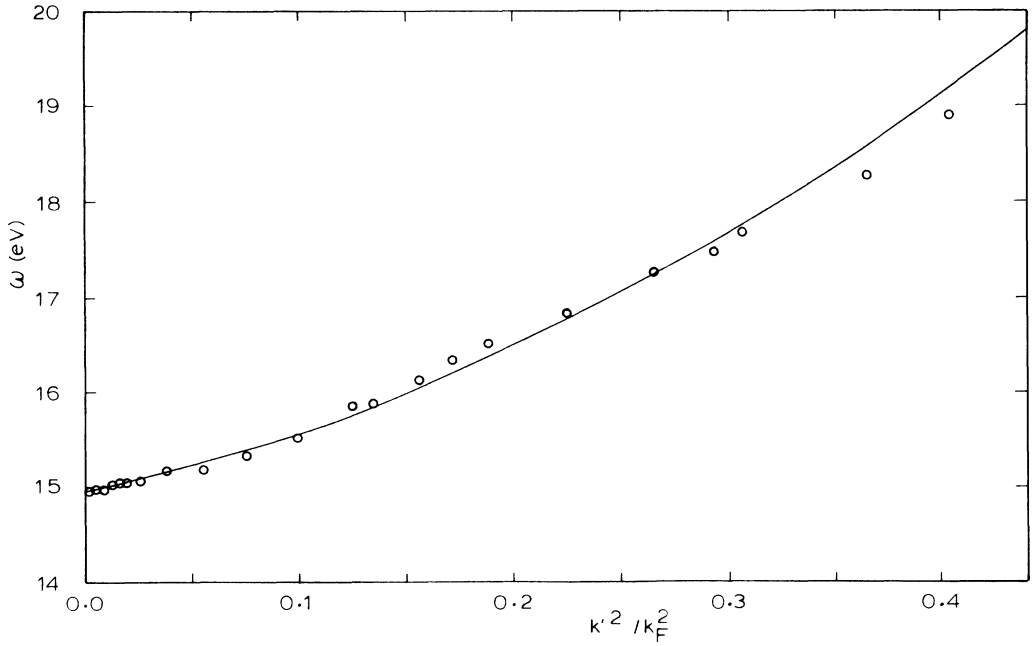

FIG. 3. Plot of plasmon energy ω vs transferred momentum squared $\mathbf{k}'^2$; transferred momentum is written in terms of Fermi momentum k_F. The line is a plot of (7) with $\omega_p = 15$ eV, $\alpha = 0.22$, and $\beta = 0.75$.

second term in (9) is negative, α given by (9) can be negative; thus we can match the negative α_m measured for Cs.[4]

For Al, and other metals, the plasmon energy increases faster than k'^2, and this increase becomes noticeable at $k'^2 \sim 0.1 k_D^2$ in a plot of ω versus k'^2. As the transferred momentum increases, the third term in (8) begins to make a significant contribution to the plasmon energy. In Fig. 3, we have replotted Fig. 2 of Ref. 1 showing the measured plasmon energy[17] as a function of transferred momentum squared. The abscissa is transferred momentum squared in terms of Fermi momentum k_F, from $\epsilon_F = 11.8$ eV; unlike Ref. 1, the ordinate is plasmon energy in electron volts. The curve in Fig. 3 is given by (8), using a measured electron plasma frequency of 15 eV,[17] measured alpha of $\alpha = 0.22$,[1] and the theoretical value of $\beta = 0.75$. We see that or new theory agrees closely with this set of measurements.

V. CONCLUSION

We have derived a plasmon dispersion relation which matches measurements in zeroth order. The theory assumes that the electron and hole of a ring diagram are trapped in a lattice wave. This trapping lowers the electron momentum below the Fermi momentum and provides a large interaction energy to make the trapped state allowable.

We expand the plasmon energy in terms of transferred momentum squared; the contribution of the RPA term to the plasmon energy is proportional to the electron momentum squared. The trapped electrons have low momentum, making the RPA contribution small. A second term of the expansion, which involves the Debye momentum, makes the significant contribution to the plasmon energy. Our theory predicts that the coefficient of this second term is an antilinear function of k_D^2/ω_p; experimental measurements of α support our theory.

Our theory is also supported by measurements of plasmon energy versus transferred momentum squared. In a plot of ω versus k'^2 using (8), with ω_p and α given by measurements and β given by theory, we match measurements made on Al. Further investigation is needed to determine whether remaining discrepancies between theory and experiment can be attributed to higher-order effects.

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