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Nonlocal electrodynamic effects in the optical excitation of the surface plasmon resonance

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Abstract

The possible nonlocal electrodynamic effects on the optical excitation of the surface plasmon resonance (SPR) at a metal–dielectric interface are studied theoretically adapting the Kretschmann attenuated-total-reflection (ATR) geometry. Calculations of the SPR reflectivity are performed using both the Lindhard–Mermin and the hydrodynamic models for the dielectric response of the metal film. The results are compared with those obtained from the classical Drude model, as well as those from previous study for a bimetallic system. It is concluded that, unlike the bimetallic system, these nonlocal effects are relatively insignificant in the Kretschmann device, except perhaps at cryogenic temperatures when appreciable changes in dip-reflectivity values can take place due to the significance of single-particle excitation.

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1. Introduction

Surface plasmon resonance (SPR) refers to the resonant collective oscillation of the free electrons at a metal–dielectric interface, and has been well understood since the early works of Ritchie and collaborators in the late 1950s [1], when experiments were limited to excitations via charged-particle beams. Although optical excitation of such modes had been observed accidentally by Wood [2]

much earlier via reflection of light from a metallic grating, systematic optical excitation of SPR was achieved only in the late 1960s via the ATR geometry by Otto [3] and Kretschmann [4]. This latter geometry which has a metal film of tens of nanometer in thickness coated onto a prism is so simple, and has been employed in various applications, ranging from optical constant measurements to sensor devices [5,6].

One of the simplest ways to monitor such optical excitation in the ATR geometry is to generate a reflectivity curve (e.g. reflectance vs incident angle or wavelength) in which a dip appears when the resonance condition is satisfied. The physical

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understanding of this phenomenon is simple in terms of the coupling of light into the electronic motions subjected to conservation of momentum along the interface, and almost all experimental observations to date can be quantitatively accounted for via the simple classical Fresnel equations, in which local dielectric response of the metal film has been assumed [6].

From a more fundamental point of view, however, all optical responses should be nonlocal in nature, in the sense that the dielectric response to the external source field depends not only on the frequency, but also on the wave vector of the incident light [7]. In fact, it has been reported previously in the literature the significance of these nonlocal effects in the SPR excitation of a bimetallic (Ag/Al) system [8]. It turns out that the “plasmon film” (Ag) can be made very thin to support the SPR in this system, and the nonlocal effects are then manifested as the film thickness becomes much smaller than the wavelength ($d \sim 0.01\lambda$). In this previous work [8], the simple hydrodynamic model has been used to account for the observed nonlocal effects.

In our present study, we shall model these effects for the more common Kretschmann geometry, using both the hydrodynamic and the Lindhard–Mermin (RPA) models. We shall see that, unlike the bimetallic system, these nonlocal effects are in general negligible in the Kretschmann geometry, as is observed in common practice. The main reason is that to excite efficiently the SPR in the Kretschmann geometry, metal film thickness of $d \sim 0.1\lambda$ has to be used and the nonlocal effects are much less evident at such film thickness. However, these effects can become significant at low temperatures when the electron mean-free-paths are much longer than the “classical skin depth” of the incident light.

2. Theoretical model

There has been an intensive theoretical study on the nonlocal optical response at an interface since the early work by Kliewer and Fuchs [9]. This includes, for example, the d -parameter theory of Feibelman [10] and that of Schaich et al. [11], as well as the more recent work by George based on an extended version of the semi-classical infinite

barrier (SCIB) model to account for the smooth variation of the electronic density across the geometrical surface [12]. Works up to the early 1980s can be found in the comprehensive review article by Feibelman [10]. While more of the works in the literature have focused on the nonlocal optics at a single interface [9–12], multilayer systems have also been studied [13–15]. One must be aware that while the generalization from a single-interface to multilayer systems is straightforward in local optics via the Fresnel theory, the same is not true in nonlocal optics since the standard boundary conditions (i.e. the continuity of various components of the field vectors) cannot be applied. For our purpose here to study the nonlocal effects in the Kretschmann geometry which involves a multilayer system, we shall adopt the SCIB theory worked out by Jones et al. [13] based on the dielectric-constant tensor approach of Kliewer and Fuchs [9]. A similar theory by Melnyk and Harrison [14] had been applied in the previous study of nonlocal effects in the bimetallic system [8]. To be self-contained, we shall first give below a brief summary of the results in [13] in our notation.

Thus, to define our Kretschmann geometry (Fig. 1), we will have a metal film of thickness $d = 2L$ for $-L \leq z \leq L$, while glass of refractive index n_0 fills the space for $z \leq -L$ and for simplicity we assume vacuum above $z \geq L$. Light (p-polarized) of frequency ω and wave vector q is incident at an angle θ in the x - z plane from the glass and the SPR is excited at the $z = L$ interface. It is well known that, at a

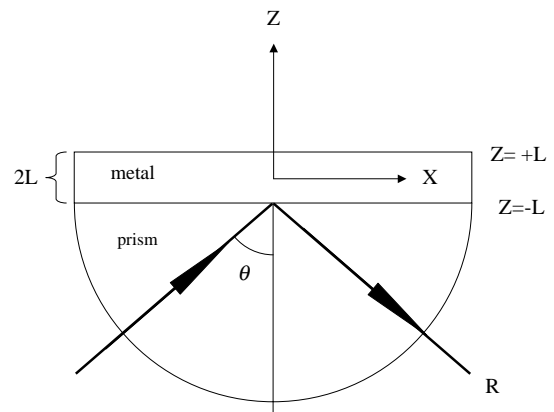


Fig. 1. Configuration of the Kretschmann geometry.

certain θ when SPR occurs, the light reflected at the $z = -L$ interface will drop to a small value due to the coupling of the incident light energy into the collective oscillation of the free electrons [6]. In the case of local dielectric response, we shall use the Drude model for the metal film and calculate the reflectivity by the usual Fresnel formula. Thus, in this case, we have the dielectric function of the metal film given by

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\omega\gamma}, \quad (1)$$

where $\omega_p = \sqrt{4\pi ne^2/m}$ is the plasmon frequency and γ the damping constant of the electron gas, respectively, with n being the number density of the electrons. In the case of nonlocal dielectric response, the reflectivity can be obtained by following reference [13] with the incident medium (vacuum in [13]) replaced by glass. In our present application, this can be expressed as

$$R = \left| \frac{Z_p - \cos \theta/n_0}{Z_p + \cos \theta/n_0} \right|^2, \quad (2)$$

where n_0 is the refractive index of the glass and the surface impedance Z_p can be expressed as

$$Z_p = U_1(-L^+) - \frac{U_2(-L^+)U_1(L^-)}{\cos \theta + U_2(L^-)}, \quad (3)$$

with U_i defined as

$$U_{1,2}(z) \equiv \frac{1}{4L} \sum_{q_z} K e^{iq_z(z \pm L)}. \quad (4)$$

Note that component wave vector q_z is quantized in the form $m\pi/2L$ and

$$\begin{aligned} U_1(L) &= U_2(-L) \equiv \frac{1}{4L} \sum_m K(-1)^m, \\ U_1(-L) &= U_2(L) \equiv \frac{1}{4L} \sum_m K. \end{aligned} \quad (5)$$

The quantity K in Eqs. (4) and (5) is defined in terms of the dielectric tensor [9]

$$K \equiv \frac{2i\omega}{c} \left(\frac{T_{zz}}{T_{zz}T_{xx} - T_{zx}T_{xz}} \right) \quad (6)$$

with $T_{ij} = (\omega^2/c^2)\varepsilon_{ij} - q^2\delta_{ij} + q_iq_j$, where $q^2 = q_x^2 + q_z^2$. The tensor T_{ij} can in turn be expressed in terms of the nonlocal longitudinal and transverse di-

electric functions $\varepsilon_\ell(\omega, q)$ and $\varepsilon_t(\omega, q)$ as follows [9,13]:

$$\begin{aligned} \varepsilon_{zz} &= \frac{1}{q^2} (\varepsilon_\ell q_z^2 + \varepsilon_t q_x^2), \\ \varepsilon_{zx} &= (\varepsilon_\ell - \varepsilon_t) \frac{q_x q_z}{q^2} = \varepsilon_{xz}, \\ \varepsilon_{xx} &= \frac{1}{q^2} (\varepsilon_\ell q_x^2 + \varepsilon_t q_z^2). \end{aligned} \quad (7)$$

We want to remark that in the limit of local response, one can show explicitly that the model presented above in Eqs. (2)–(7) does reduce to the standard result given by the Fresnel equations (see Appendix A).

In order to calculate the nonlocal SPR reflectivity from Eqs. (2)–(7), we shall adopt the Lindhard–Mermin model for ε_ℓ and the simple Lindhard model for ε_t as was done in the previous literature [12,16]. To compare with previous results for the bimetallic system [8], we have also performed the calculation using the hydrodynamic model for ε_ℓ and the simple Drude model for ε_t , respectively. Detailed expressions of these models are well-available in the literature [16]. It may be of interest to note that similar comparative study has been performed previously on the absorbance of metallic-insulator superlattice [16] as well as on the static multipole polarizability of nanoparticles [17].

3. Numerical results

We have applied the above model to a Kretschmann geometry with a silver (Ag) film. Though it is well known that the free-electron model is an oversimplified description for Ag since the interband transitions from the s and d electrons (and their mutual interaction) are ignored, it does provide an acceptable qualitative account for the behavior of the plasmons in the metal [18]. Since our goal here is mainly to demonstrate the nonlocal effects *relative* to the local ones, we have thus adopted the free-electron model for its simplicity. Besides, we are also interested to make contrast with the previous work [8] on the bimetallic (Ag/Al) system in which the authors had also used the Drude and hydrodynamic models

(together with an added empirical local term for the d-electron interband transitions). Indeed, there exist in the literature more accurate dielectric functions for Ag, both semi-empirical ones [19] and purely theoretical ones [20], but for our purpose of illustrating the nonlocal effects, we shall adopt the simplest possible approach. We believe that the qualitative features of these effects obtained here will remain valid when more accurate

models are used, this is substantiated by previous experiments with Ag in which the free-electron models were used as a comparison with the data [18].

Fig. 2 shows the results for the SPR reflectivity (R) versus the incident angle at fixed optical frequencies for three different metal (Ag) film thickness. It is observed that while the nonlocal effects are quite insignificant at frequency much lower

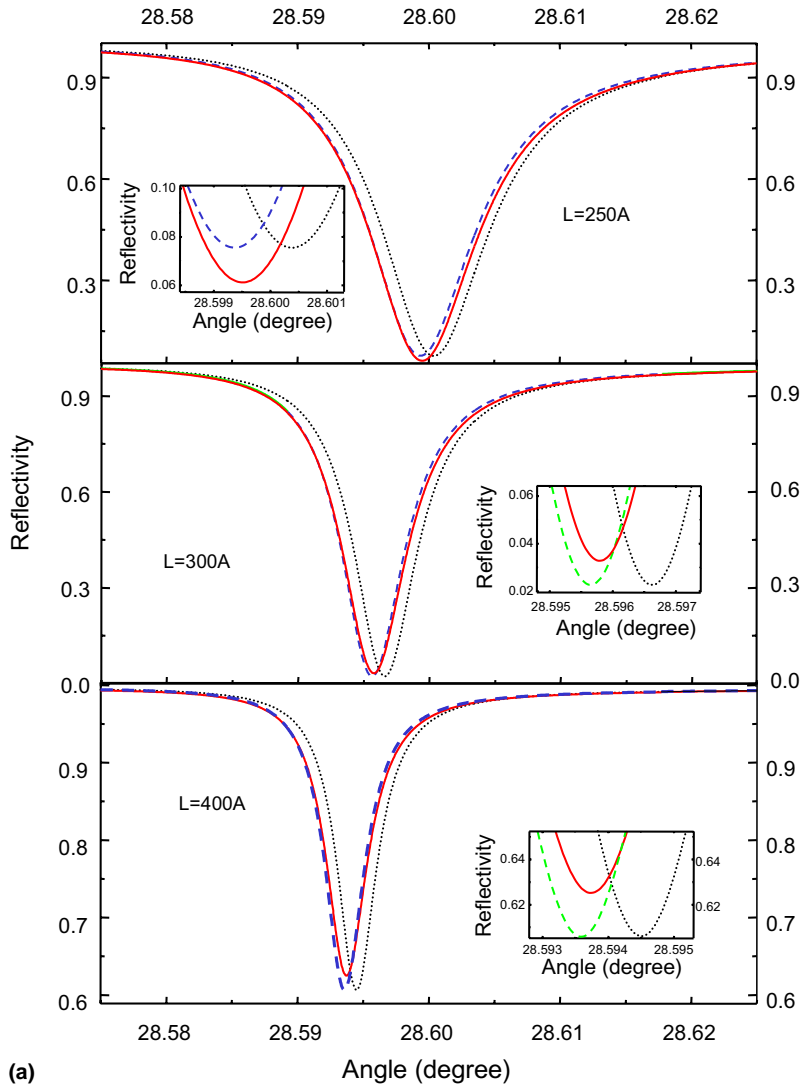


Fig. 2. (a) SPR reflectivity versus incident angle for three different metal film thickness according to the three models: Drude (dotted line), hydrodynamic (dashed line), and Lindhard–Mermin (solid line). The damping constant is set at $\gamma = 0.001\omega_p$ and the source frequency at $\omega = 0.1\omega_p$. (b) Same as (a), but for frequency $\omega = 0.5\omega_p$.

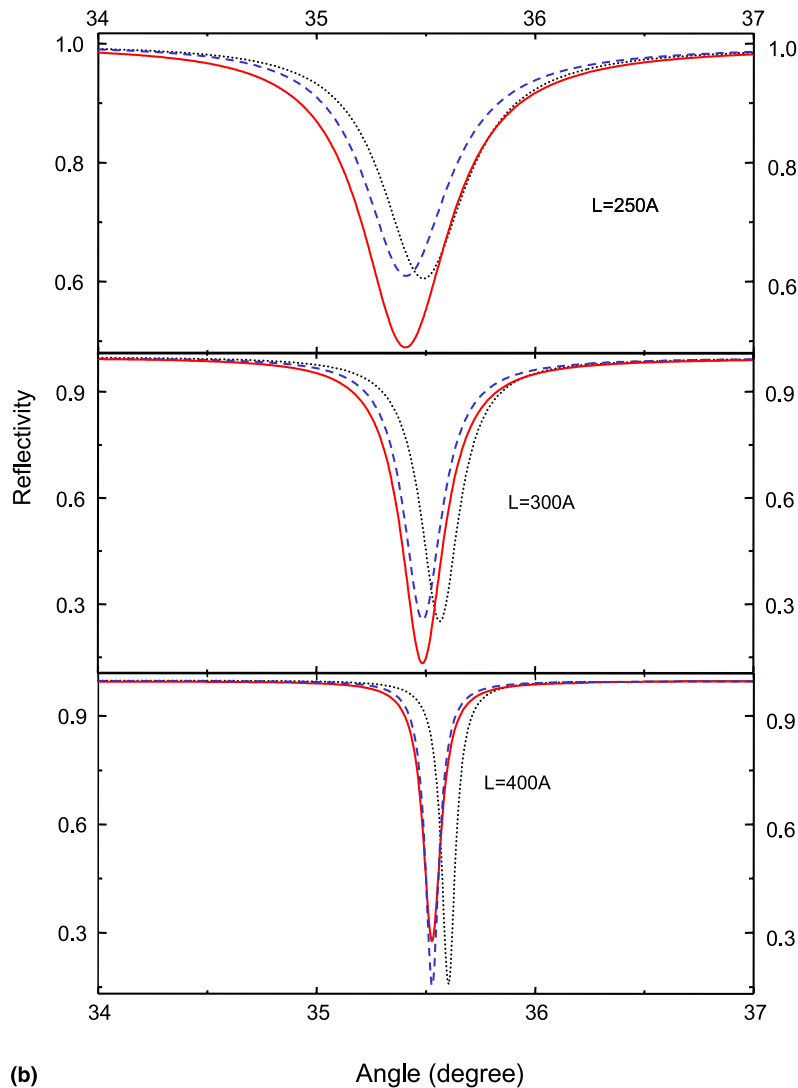


Fig. 2. (continued)

than the SPR frequency in Fig. 2(a), they can be significant when close to the SPR frequency as in Fig. 2(b) where $\omega = 0.5\omega_p \approx 0.7\omega_{sp}$. This is in contrast to the previous study of such effects on the polarizability of nanoparticles, where they were found to be significant even at off-resonant frequencies [17]. In addition, one observes that although the hydrodynamic (H) model gives results very close to the Drude (D) model in all the cases (except for a small shift of the “dip angle” to

a lower value due to the nonlocal effects on the dispersion relation), the Lindhard–Mermin (LM) model gives significantly different values for the “dip reflectivity” up to 10% below or above the local values from the D model depending on the thickness of the metal film. Similar results can be seen from Fig. 3, where a spectral plot of R as a function of the incident wavelength shows the same distinct behavior for the LM model with reference to the dip-reflectivity values. The

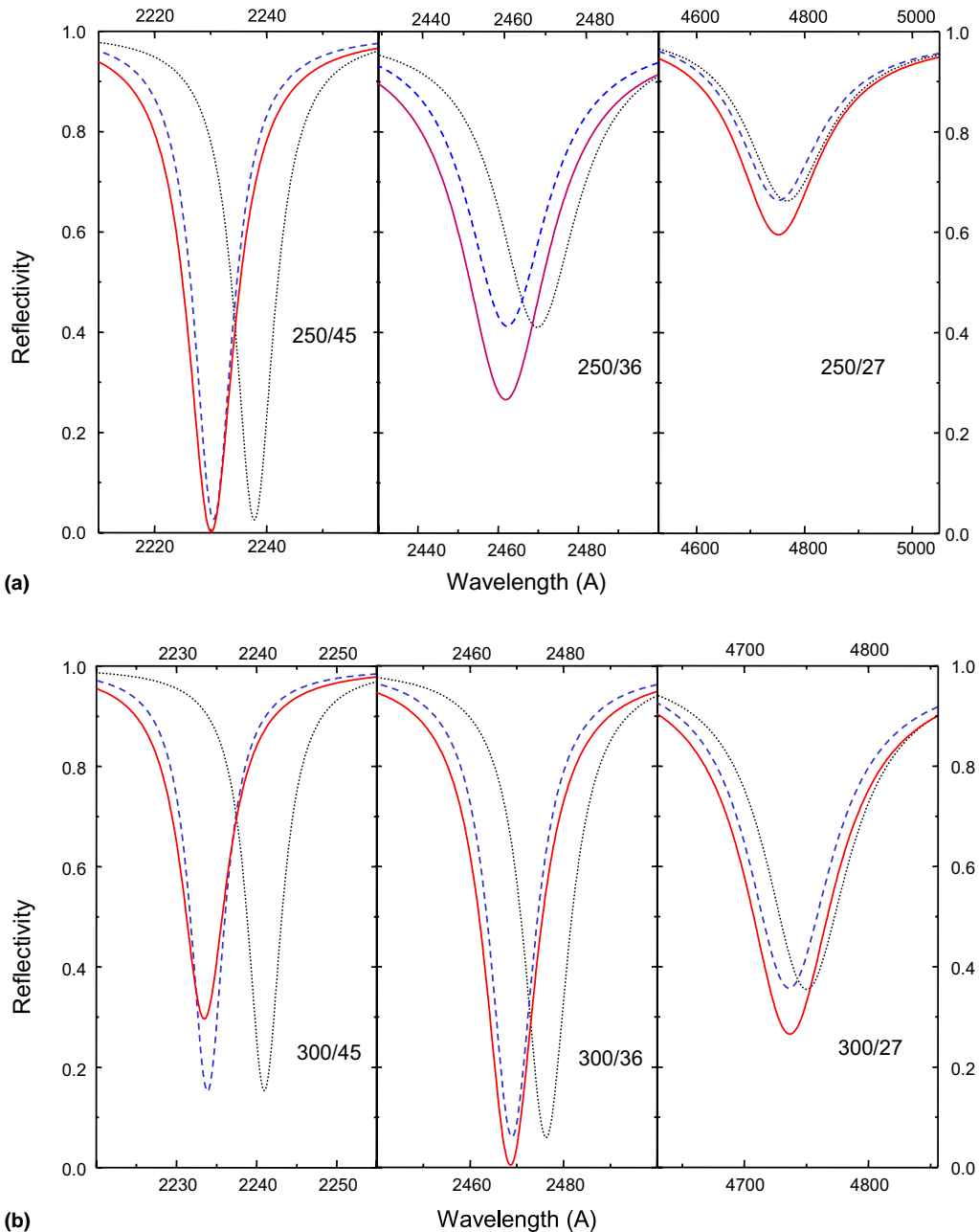


Fig. 3. (a) Spectral plot of the SPR reflectivity at three different values of the incident angle ($\theta = 27^\circ$, 36° , and 45°) for a metal film thickness of 50 nm (i.e. $L = 250 \text{ \AA}$). The results from the three models are illustrated in the same way as in Fig. 1. (b) Same as (a), but for a film thickness of 60 nm (i.e. $L = 300 \text{ \AA}$). (c) Same as (a), but for a film thickness of 80 nm (i.e. $L = 400 \text{ \AA}$).

nonlocal dispersion relations in both the H and LM models again lead to a slight ($<0.5\%$) “blue-shift” in the resonance (dip) wavelength, as was

observed previously [8]. In addition, the H and D models yield very close values for R in all cases. Note that the resonance occurs at relatively short

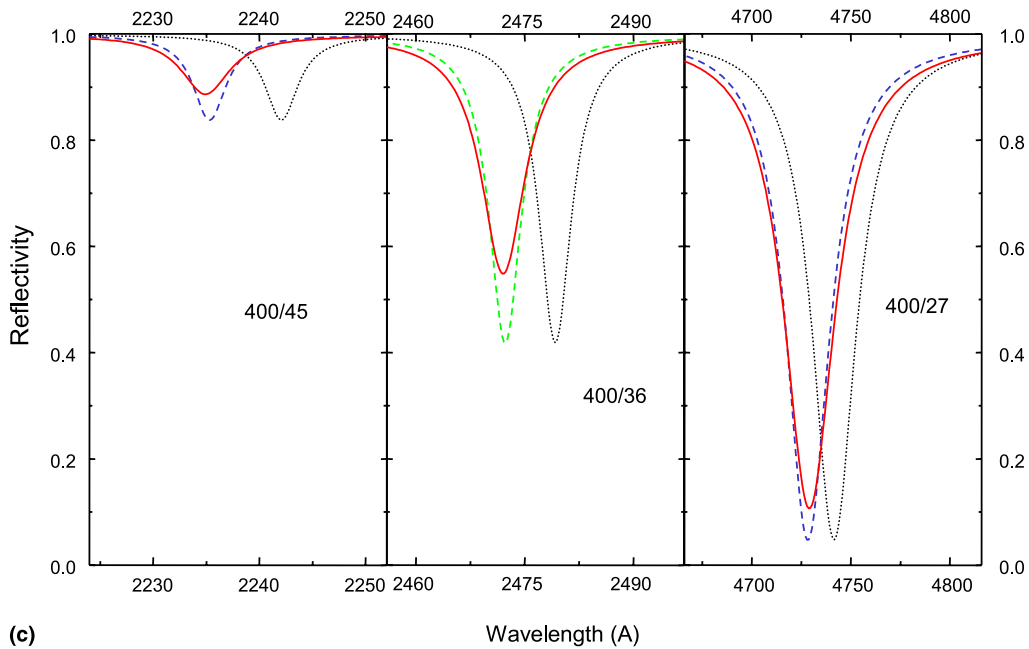


Fig. 3. (continued)

wavelengths since in this model calculation we have taken the plasmon energy for silver to be ~ 9 eV [8].

These results can be understood in terms of the fact that while the H model accounts for mainly the collective (plasmon) motion of the electrons in the metal, the LM model accounts for, in addition, also the single-particle (e–h pair) excitation which can be important for large values of the wave vector [15–17]. Thus the closeness between the results obtained in the D and H models indicate that nonlocal effects are quite insignificant in the surface plasmon excitation in the Kretschmann geometry. However, for the LM model, the e–h pair excitation will provide a “competing mechanism” for the surface plasmon excitation as follows. For smaller thickness (e.g. $d = 2L = 50$ nm), the LM model turns out to couple more light into the SPR excitation at the metal–vacuum interface via the well-known anomalous skin effect [21], leading to SPR dips lower than those obtained in the D and H models. For larger thickness, however, the effect due to the e–h pair excitation can lead to a decrease in the coupling of incident light to the SPR

excitation resulting in an overall increase in the dip-reflectivity value.

Fig. 4 shows the dip-reflectivity value as a function of the damping constant (γ) in the various dielectric response function in the three models. It is seen that the results are again quite sensitive to the value of the film thickness. Within the range of damping considered, one can switch from a monotonic decrease dependence of R on γ to a reverse trend for different film thickness. We again understand this in terms of two mechanisms: the absorption (determined by γ) of the incident light inside the film and the coupling of this to the excitation of the SPR at the vacuum–metal interface. While both will result in a decrease in the reflectance, the suppress in the coupling of the SPR can lead to an overall increase of R for a thicker metal film. For the thinner film, such an increase trend will have to occur at much greater values of γ (e.g. this occurs for $\gamma > 0.008\omega_p$ for the $L = 250$ Å film). In addition, it is seen once again that the LM model behaves quite different compared to both the D and H models due to its account for the e–h pair excitation.

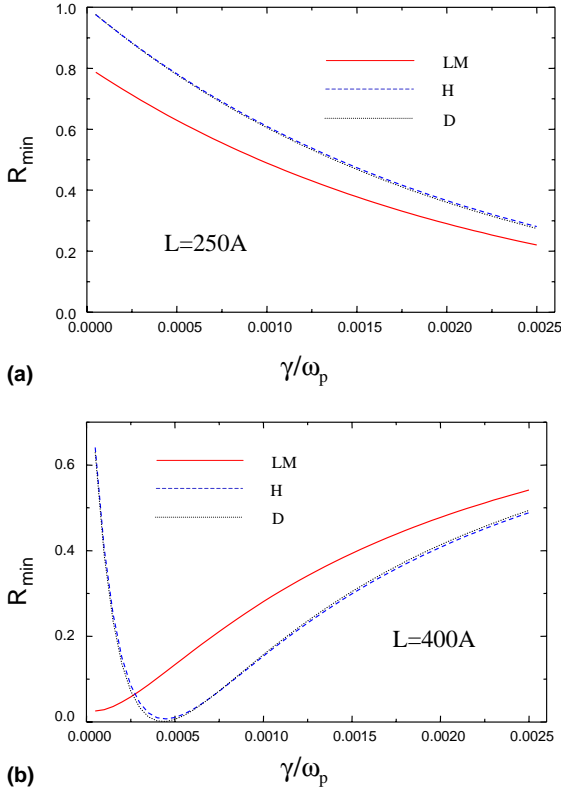


Fig. 4. (a) Dip-reflectivity versus the damping constant for the three models at $\omega = 0.5\omega_p$ for film thickness of 50 nm. The incident angle is fixed at values close to the “dip position” (35.49° for Drude model and 35.41° for both the hydrodynamic and LM models). (b) Same as in (a), but for a film thickness of 80 nm.

4. Conclusion

From a comparative study, we conclude that the nonlocal optical effects are relatively insignificant in the Kretschmann ATR geometry for the optical excitation of SPR at a metal–dielectric interface. This is based on the closeness between the results obtained from the D and H models in all our computations. The distinction between the two in both the angular and spectral reflectivity is less than 0.5% in the dip position, though it may become possible to observe this difference in the spectral case with high-resolution spectrometer.

Moreover, to exhibit large difference in both the dip value and dip position between the D and H models, one has to use very thin metal film thickness ($L \sim 2$ nm), in which the SPR cannot be ef-

ficiently excited in the Kretschmann geometry (e.g. with $R_{\text{dip}} > 95\%$). This is in contrast to the bimetallic system studied previously in which the plasmon (Ag) film is made very thin (< 10 nm) where such effects were found to be important, and significant difference was observed between the local and the hydrodynamic models [8].

Moreover, the deviation between the LM model and the other two models in the dip-reflectivity values is significant even at reasonable metal film thickness commonly used in the Kretschmann geometry (say, $d \sim 50$ nm). We believe that this is possibly observable at low temperatures when the electronic mean free paths become much longer than the “classical skin depth” of the incident light [21]. Such a cryogenic SPR experiment will be of interest, and may open up new applications of the SPR towards temperature sensing, as has already been in practice in the monitoring of substrate heating effects at elevated temperatures [22].

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Appendix A

To obtain the local limit of the ATR reflectivity given in Eqs. (2)–(7), we observe that in this limit, $\varepsilon_\ell = \varepsilon_t \equiv \varepsilon$ is independent of the wave vector and Eq. (7) simplifies to the following:

$$\begin{aligned} \varepsilon_{zz} &= \varepsilon, \\ \varepsilon_{xx} &= \varepsilon, \\ \varepsilon_{zx} &= \varepsilon_{xz} = 0. \end{aligned} \quad (\text{A.1})$$

It follows from Eq. (6) that

$$K = \frac{2i\omega}{c} \frac{Q^2}{(\omega^2/c^2)\varepsilon(Q^2 - q_z^2)} \quad (\text{A.2})$$

with

$$Q^2 \equiv \frac{\omega^2}{c^2} \varepsilon - q_x^2. \quad (\text{A.3})$$

As a result, Eq. (5) becomes

$$U_1(L) = U_2(-L) \equiv \frac{iQ^2}{2L\varepsilon(\omega/c)} \sum_{q_z} \frac{(-1)^m}{Q^2 - (m\pi/2L)^2},$$

$$U_1(-L) = U_2(L) \equiv \frac{iQ^2}{2L\varepsilon(\omega/c)} \sum_{q_z} \frac{1}{Q^2 - (m\pi/2L)^2}. \quad (\text{A.4})$$

By using

$$\cot z = \sum_m \frac{1}{z + m\pi}, \quad (\text{A.5})$$

and with some manipulation, Eq. (A.4) can be further simplified to

$$U_1(L) = U_2(-L) = \frac{iQ}{\varepsilon(\omega/c) \sin(2QL)},$$

$$U_1(-L) = U_2(L) = \frac{iQ}{\varepsilon(\omega/c)} (2QL). \quad (\text{A.6})$$

Substituting $U_{1,2}(\pm L)$ into Eq. (3), we obtain the reflectivity from Eq. (2) as

$$R = \frac{r_{gm} + r_{mv} e^{4iQL}}{1 + r_{gm} r_{mv} e^{4iQL}}, \quad (\text{A.7})$$

where

$$r_{gm} = \frac{k_{zg}/\varepsilon_g - Q/\varepsilon}{k_{zg}/\varepsilon_g + Q/\varepsilon} \quad (\text{A.8})$$

and

$$r_{mv} = \frac{Q/\varepsilon - k_{zv}/\varepsilon_v}{Q/\varepsilon + k_{zv}/\varepsilon_v}. \quad (\text{A.9})$$

In Eqs. (A.8) and (A.9), $\varepsilon_{g(v)}$ and $k_{zg(zv)}$ are, respectively, the dielectric constant and z -component wave vector in glass (vacuum), respectively. Eqs. (A.7)–(A.9) lead back to the reflectivity exactly the same as that obtained from the local theory of Fresnel optics [6].

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