Non-local effects in the plasmons of strongly interacting nanoparticles, dimers, and waveguides

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Non-local effects in the optical response of noble metals are shown to produce significant blueshift and near-field quenching of plasmons in nanoparticle dimers, nanoshells, and thin metal waveguides. Compared with a local description relying on the use of frequency-dependent dielectric functions, we predict resonance shifts as large as 10% and field-intensity reduction of an order of magnitude at inter-particle distances or metal thicknesses below 2 Å. Our results are based upon the specular-reflection model combined with a suitable non-local extension of measured local dielectric functions. We present a roadmap to design plasmon resonances in nanometer metallic elements with application to optical antennas and improved photovoltaic, light-emitting, and sensing devices.

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Knowledge of the optical response of materials at the nanoscale has become a pillar of nanophotonics. While excellent agreement between theory and experiment is generally achieved for nanoparticles and nanostructured materials by relying on local, frequency-dependent dielectric functions [1, 2], non-local effects are known to play an important role at small distances in the few- or sub-nanometer region [3]. This range of distances is becoming experimentally feasible in metallic dimers [4], nanoshells [5], and tips [6], which exhibit large near-field enhancement [7, 8] with practical application to improved SERS biosensing [6, 9], photovoltaics [10], and solid-state lightning [11]. However, no account of non-local effects has been reported in such systems, due in part to the complexity of non-local descriptions of the optical response in inhomogeneous environments.

First-principles calculations of the optical response are only available for relatively simple systems, such as bulk metals and small clusters of noble metal atoms [12]. However, several approximate prescriptions have been elaborated to deal with more complicated systems, and most notably the $d$–function formalism of Feibelman [13] and the specular reflection model (SRM) [14, 15, 16]. The latter is particularly advantageous because it permits expressing the response of bounded homogeneous media in terms of their non-local bulk dielectric function, as already reported in studies of fast electrons and ions moving near planar surfaces [17].

In this Letter we carry out SRM calculations of dimers, shells, and thin waveguides made of gold and silver. We show that non-local effects produce significant plasmon blueshifts and reduction of the near-field enhancement. The response is constructed from measured optical constants, which are extended to include non-local effects in the contribution of valence electrons. The validity of this model is corroborated by successfully explaining experimentally observed quantum-confinement effects leading to broadening and blueshift of plasmons in small metal particles. We draw conclusions on more complicated systems of relevance in plasmonics by applying the same model.

A first example of the blueshift produced by non-locality is shown in Fig. 1 for scattering spectra of gold dimers calculated with (solid curves) and without (dashed curves) inclusion of non-local effects. The shift becomes more apparent as the inter-particle distance is reduced and it is accompanied by sizeable plasmon broadening. This lowest-order longitudinal dipole mode of the dimer involves huge piling up of induced charge in the particle junction region [8], thus enhancing the role of non-locality.

In the SRM used throughout this work, each interface separating two homogeneous media is described by surface charge distributions on either side. These surface charges are used to construct boundary fields as if they were surrounded by an infinite homogeneous medium. The surface charges are determined by imposing the continuity of the electric potential and the normal displacement across the interface [17]. The response of the inhomogeneous system is thus reduced to the knowledge of non-local bulk dielectric functions of the materials involved.

Homogeneous media are conveniently described in momentum space $q$, in which non-locality shows up as a dependence of the dielectric function $\epsilon(q, \omega)$ on $q$. In general insulators behave as local media, whereas delocalized $s$ valence electrons in noble metals constitute a source of non-locality. It is thus reasonable to treat the response of both insulators and core-polarization in metals as local and to approximate the valence-electron contribution in the $q \to 0$ limit by a Drude formula, $\epsilon(D)(\omega) = 1 - \omega_p^2/(\omega^2 + i\eta)$, where $\omega_p$ is the valence-electron-gas plasma frequency and $\eta$ is the plasmon width. Delocalized valence excitations produce a significant $q$ dependence, as studied by Lindhard in the so-called random-phase approximation (RPA) [18], and later by Mermin to include electron-motion damping in a self-consistent fashion [19]. We adopt here the dielectric function pro-
posed by Mermin $[\epsilon^M(q,\omega)]$ to describe the full non-local contribution of valence electrons. This function has the desirable $q \to 0$ limit $\epsilon^M(0,\omega) = \epsilon^D(\omega)$. The resulting non-local permittivity of the metal is thus approximated by $^{20}$

$$\epsilon(q,\omega) = \epsilon^{\text{loc}}(\omega) - \epsilon^D(\omega) + \epsilon^M(q,\omega), \quad (1)$$

where $\epsilon^{\text{loc}}(\omega)$ is the local, frequency-dependent part of the response, taken from optical measurements $^{21}$. We correct the latter in Eq. (1) by subtracting the local valence-electrons contribution $\epsilon^D$ and adding the non-local valence-electrons response $\epsilon^M$. Finally, $\omega_p$ and $\eta$ are chosen to fit both the long-wavelength tail and the observed plasmon frequency of $\epsilon^{\text{loc}}$ $^{22}$ ($\hbar\omega_p = 9$ eV and $\hbar\eta = 0.05$ eV for gold; $\hbar\omega_p = 9.1$ eV and $\hbar\eta = 0.02$ eV for silver).

The momentum and distance dependence of the response of bulk gold is represented in Fig. 2. In particular, Fig. 2(a) shows the so-called loss function of gold $[\text{Im}\{-1/\epsilon(q,\omega)\}]$ under the approximation of Eq. (1), which is directly accessible to electron energy-loss spectroscopy $^{23}$. Non-local effects become dramatic in the optical region for $q \gtrsim 1$ nm$^{-1}$ (i.e., to the left of the Landau cutoff for excitation of valence electron-hole pairs, $\omega = qv_F$, where $v_F$ is the Fermi velocity), involved in plasmonic structures. Actually, the real-space response $V^{\text{non-loc}}$ obtained from the Fourier transform of $4\pi/[q^2\epsilon(q,\omega)]$ differs considerably from the local approximation $V^{\text{loc}} = 1/[r\epsilon^{\text{loc}}(\omega)]$ up to distances above $\sim 1$ nm [Fig. 2(b)]. The ratio between these two quantities has a real part significantly smaller than 1 over that range of distances, while the imaginary part lies below 0.2 in modulus within the area explored in Fig. 2(b).

It is useful to apply this formalism to spherical particles, the optical response of which is conveniently described by their multipolar response to external potentials of radial dependence $r^l$, which develop an induced potential $-\alpha_l/r^{l+1}$, where $l$ is the orbital momentum number and $\alpha_l$ is the polarizability of order $l$. Applying the SRM, one finds $^{10}$

$$\alpha_l = a^{2l+1} \frac{\ell_l - \ell_h}{\ell_l + (l+1)\ell_h}. \quad (2)$$

![FIG. 1: Extinction spectra of dimers formed by spherical gold particles of 20-nm in diameter. Local (broken curves) and non-local (solid curves) calculations are compared for several separations between the particle surfaces, $d$. Consecutive curves are offset vertically by 500 nm$^{-2}$ for clarity. The external electric field is parallel to the inter-particle axis.](image)

![FIG. 2: (a) Non-local wavelength- and momentum-dependent response function of homogeneous gold. (b) Distance dependence of the non-local interaction potential derived from (a) and normalized to the local potential $1/[r\epsilon^{\text{loc}}(\omega)]$.](image)

![FIG. 3: Extinction spectra of spherical gold particles embedded in glass ($\varepsilon = 2.3$). The present non-local theory (dashed curves) is compared to experiment (solid curves, taken from Ref. [3]) for various values of the particle diameter (see text insets). The calculated spectra have been shifted 15 nm to the red to improve comparison.](image)
including all multipoles with multiple scattering to obtain the self-consistent field [24], by the polarizabilities of Eq. (2) and then perform multiple scattering to obtain the self-consistent field [24]. This agreement between experiment and theory supports our approach to describe non-local and theory supports our approach to describe non-local metal behavior at short distances.

For particle dimers [Fig. 1] we describe each sphere by the polarizabilities of Eq. (2) and then perform multiple scattering to obtain the self-consistent field [24], including all multipoles with \( l \leq 20 \) to achieve convergence. The dependence of the lowest-order dipole-mode wavelength on inter-particle separation in gold and silver dimers is shown in Fig. 1 with (solid curves) and without (dashed curves) inclusion of non-local effects. Besides significant blueshifts, non-locality increases the plasmon broadening (shaded areas), an effect that we attribute to the availability of additional loss channels (valence electron-hole pairs) in the metallic response.

Accompanying the far-field phenomenology discussed above, the near field is also influenced by non-local effects, which can reduce the field enhancement at the center of a dimer by nearly an order of magnitude, as shown in Fig. 1. This limits the applicability of metal structures to SERS and non-linear optics, as compared with the expectations opened by the field enhancement predicted in the local approximation. Again, losses originating in electron-hole-pair excitations contribute to this reduction, and so does the finite penetration of the induced charge towards the interior of the metal by a distance \( \sim v_F/\omega \) [17] (see Fig. 2). This is in contrast to the vanishing penetration associated to local descriptions.

Finally, non-local effects are not exclusive of small particles or inter-particle gaps. They are also important in other strongly-interacting metallic geometries typically encountered in plasmonics like nanoshells [Fig. 2(a)] and waveguides [Fig. 2(b)]. Similar to dimers, the plasmon modes in these structures undergo blueshifts exceeding 10% at thicknesses below 5 Å. Interestingly, the mutually complementary geometries of the dielectric gap and the metal film considered in Fig. 2(b) should yield the same dispersion relation in the non-retarded limit (dashed curve), but non-local effects produce different dispersion relations for each of these systems.

where \( \frac{1}{\epsilon_i} = \frac{2a}{\pi(2l+1)} \int_0^\infty dq \frac{\epsilon(q, \omega)}{\epsilon(q, \omega)} j_l(qa) \), \( \epsilon \) is the particle radius, \( \epsilon_h \) is the permittivity of the local host medium surrounding the particle, and \( j_l \) is the spherical Bessel function of order \( l \).

Fig. 3 shows good agreement because the present non-local calculations (broken curves) and experimental data [3] (solid curves) for light scattering by small gold particles. Quite different from the size-independent spectral profiles predicted by a local description, non-local effects give rise to significant broadening for particle radius below 2 nm [cf. Fig. 2(b)]. These are the so-called quantum confinement effects, which show up when the mean free path of valence electrons is comparable to the particle diameter [3]. This agreement between experiment and theory supports our approach to describe non-local metal behavior at short distances.

FIG. 4: Dimer dipole-plasmon wavelength as a function of inter-particle surface spacing \( d \) for gold (a) and silver (b) 20-nm nanoparticles. Solid and broken curves correspond to non-local and local descriptions of the metal, respectively. The width of the modes is represented by shaded regions covering the FWHM span of the scattering-cross-section plasmon peaks.

More elaborate methods have also been used to describe non-locality, particularly using density-functional theory [12] and plasmon quantum models [25], although they become impractical in large systems or non-trivial geometries. In contrast, the SRM used here accounts for the main features of non-locality and is sufficiently versatile to deal with relatively complex systems like those discussed above.

In summary, we have shown that non-local effects are relevant in the response of metal systems involving short distances below a few nanometers. In particular, we have reported large blueshifts and reduced near-field intensity compared to a local description in metallic dimers, nanoshells, and thin films. These effects should be important in the design of plasmonic elements on the nanometer scale, for which the formalism provided here provides a suitable and versatile framework.

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FIG. 5: Enhancement of the electric field intensity relative to the incident field ($|E/E^\text{ext}|^2$) at the center of metallic dimers with the same dimensions as in Fig. 4 (see point P in the inset of that figure). (a) Spectral dependence of the enhancement for various separations between the surfaces of 20-nm spherical gold particles. (b) Maximum field enhancement as a function of separation for gold and silver dimers. The results from local and non-local descriptions of the response are shown by solid and dashed curves, respectively.

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