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Influence of Dielectric Function Properties on the Optical Response of Plasmon Resonant Metallic Nanoparticles

by

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Abstract

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The optical properties of plasmon resonant metallic nanoparticles are of great interest because of their ability both to control optical fields on the nanometer scale and to function as sensitive indicators of their local environment. I investigate the relationship between the dielectric function of a metal and the optical properties of the constituent metallic nanoparticle. Using a Drude shell — silica core nanoshell geometry, I examine how systematic changes in the parameters of the Drude dielectric function affect the near and far field properties of the nanoparticle. The nanoshell geometry allows separation of intrinsic properties and extrinsic phase retardation, or finite size, effects.
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Chapter 1

Introduction

The optical properties of metallic nanoparticles are important because of their ability to interact strongly with optical fields over length scales smaller than the diffraction limit and because they are sensitive to changes in their local environment. The dependence of the optical properties of metallic nanostructures on size, shape, and nanoenvironment is an extremely active area of research. Our increased understanding of how metallic nanostructures manipulate light is leading to applications such as nanoscale plasmon waveguides [4], a variety of nanosensing modalities [9, 11, 16, 18–20, 29, 30], and even photothermal cancer therapy [22]. Exploring how the dielectric function of the metal affects the optical overall properties of a metallic nanostructure has historically focused on experimental investigations where colloids of various metals and alloys have been synthesized and characterized [14]. In this thesis, I systematically examine the relationship between the dielectric function of the metal itself and the optical properties of its constituent nanostructure.

In the context of this study, my focus is on the properties of the metal in a hollow shell, or nanoshell, geometry illustrated in Fig. 1.1. The optical resonances of a nanoshell are sensitively dependent on the inner and outer dimensions of the metallic shell, and exhibit an enhanced sensitivity to its local dielectric environment relative to a solid spherical
Figure 1.1: Nanoshell geometry: $r_1$ is the core radius and $r_2$ is the overall shell radius.

nanoparticle [26, 28, 30]. These properties can be explained in terms of plasmon hybridization, where the plasmon excitations supported by a shell structure arise from the interaction between the plasmons on the inner and outer surfaces [25, 27]. The properties of these hybrid plasmons are also dependent upon the absolute size of the nanostructure for their linewidth [33] and for the relative contributions of absorption and scattering to the absolute far field extinction of the nanoparticle [21].

## 1.1 Dielectric Functions

The complex dielectric function of a material, denoted $\varepsilon = \varepsilon' + i\varepsilon''$, describes a material's response to an applied electric field. $\varepsilon'$ determines the degree to which the material polarizes in response to an applied field, while $\varepsilon''$ controls the relative phase of this response with respect to the applied field. A phase difference between the response and applied field results in destructive interference, thereby removing energy from the applied field. Intrinsic loss mechanisms (e.g.: electron scattering) of a material are all condensed into $\varepsilon''$. The dielectric function is related to the complex index of refraction by $\tilde{n} = n + ik = \sqrt{\varepsilon}$, where $n$ is factor by which the speed of light is reduced in the material and $k$ is the decay constant for an electric field penetrating the material. For the noble metals at optical frequencies, the dielectric function can be expressed as the sum

$$\varepsilon(\omega) = 1 + \chi_\infty + \chi_D(\omega), \quad (1.1)$$
where the background susceptibility $\chi_\infty$ arises from the core electron polarizability and interband ($d \rightarrow sp$) transitions, and $\chi_D$ is the Drude response of the conduction electrons. The background polarizability and free space response are often combined into $\varepsilon_\infty = 1 + \chi_\infty$. The Drude model is the solution of the classical equations of motion for a free electron, under the influence of an external electric field, experiencing inelastic scattering events on a characteristic time scale $1/\Gamma$. The collective behavior of the electrons in the material under consideration is then assumed to be the sum of the behavior of the individual electrons in a unit volume. Solving this model results in

$$
\chi_D(\omega) = -\frac{\omega_p^2}{\omega^2 + i\Gamma \omega}
= -\frac{\omega_p^2}{\omega^2 + \Gamma^2 + \frac{i\omega_p^2\Gamma}{\omega(\omega^2 + \Gamma^2)}}.
$$

(1.2)
where $\omega_p$ is the bulk plasma frequency and $\Gamma$ is the reciprocal electron relaxation time. In the visible and near-IR, $\Gamma \ll \omega$, therefore

$$\chi_D(\omega) \approx -\frac{\omega^2}{\omega_p^2} + i\frac{\omega^2}{\omega^3} \Gamma.$$ \hspace{1cm} (1.3)

The parameters used for the shell material in this paper, approximating the experimental Au dielectric function [13], are: $\chi_\infty = 8.5$, $\omega_p = 1.36 \times 10^{16}$ rad s$^{-1}$, and $\Gamma = 1.05 \times 10^{14}$ rad s$^{-1}$ (Fig. 1.2). The nanoshells have a silica core ($\varepsilon = 2.04$) and are embedded in free space ($\varepsilon = 1$).

Physically, $\chi_\infty$ and $\Gamma$ can be influenced in a multitude of ways. For example, there is evidence suggesting that $\chi_\infty$ and $\Gamma$ change when a polycrystalline sample is immersed in a liquid or gas that penetrates the gaps between crystal domains [5, 7, 8, 32]. Species absorbed on the surface, impurities, geometric features smaller than the electron mean free path, and even material voids may influence $\Gamma$; however this is currently poorly understood and a topic of significant debate [1, 7, 8, 10, 15, 23, 24, 26, 33].

1.2 Plasmons

The most striking optical property of metallic nanoparticles in the visible and near infrared are plasmon resonances. Plasmons are collective oscillations of the conduction electrons in a metallic material. The surface polarization due to the motion of the conduction electrons provides the restoring force on the electrons. Plasmons are sensitive to the surrounding dielectric medium because the instantaneous polarization of the medium in response to an applied field will shield surface charge, reducing the restoring force experienced by the plasmon. The intrinsic features of the plasmon resonances in a nanoshell are described by the plasmon hybridization model, illustrated in the left panel.
Figure 1.3: Plasmon hybridization model for nanoshells. (left) Dipolar spherical cavity and solid sphere plasmons hybridize, forming dipolar antisymmetric and symmetric nanoshell plasmons. (right) Schematic diagram of the charge distribution for the dipolar and quadrupolar plasmon resonances.

of Fig. 1.3 [25, 27]. In this model, separate solid sphere and spherical cavity plasmon resonances interact, or hybridize, producing a high energy antisymmetric resonance denoted $\sigma_+$ and a low energy symmetric resonance denoted $\sigma_-$. Both the sphere and cavity plasmons are expanded into an orthogonal set of multipolar modes of angular momentum $l$. The charge distributions of the dipole ($l = 1$) and quadrupole ($l = 2$) plasmons are illustrated in the right panel of Fig. 1.3. Phase retardation, illustrated in Fig. 1.4, due to the finite size of the nanoparticle with respect to the spatial extent of the wavelength of light at the plasmon resonance, causes an asymmetry in these modes along the direction of propagation of the incident wave. Interaction due to the resulting slight spatial overlap between modes of different $l$ is suppressed by the difference in energy between the modes and thus, to a good approximation, the nanoshell plasmons are described by a unique angular momentum. Phase retardation does, however, allow $l > 1$ modes to interact with light because the plasmon and light overlap energetically [6, 14]. The intrinsic properties of the plasmon resonance of a nanoshell are scale independent, determined by the material composition and the core to shell ratio $r_1/r_2$ [25]. The extrinsic properties are due to phase retardation. That is, the extrinsic properties are due to the inhomogeneity of the
electromagnetic field to which the plasmon is coupled. To use the language of solid-state physics, the extrinsic properties of the plasmon are due to it’s polaritonic character arising from the coupling of the plasmon to photons [6]. Nanoshells are uniquely suitable for this study because, unlike solid nanospheres, both intrinsic and extrinsic properties can be varied independently by controlling the core to shell ratio $r_1/r_2$ and the overall particle size, respectively.

![Diagram](image)

Figure 1.4: The spatial variation of the incident electric field due to phase retardation compared with a small and a large nanoshell.

1.3 Calculations

Near and far field optical properties of nanoshells were obtained using Mie scattering theory for coated spheres [1–3, 14]. The far field properties are described by the scattering, absorption, and extinction cross sections. The scattering cross section, $\sigma_{\text{sca}}$, is the area of the incident beam redirected away from its direction of propagation. Absorption ($\sigma_{\text{abs}}$) and extinction ($\sigma_{\text{ext}}$) cross sections are likewise defined as the area removed from the incident beam due to absorption by the particle and the total area removed by the particle, respectively. Efficiencies, defined as the cross section normalized to the particle's physical cross-sectional area, are used to facilitate comparison between particles of
different sizes. The near field enhancement, $|E|$, is the scattered electric or magnetic field at the nanoparticle surface normalized to the incident field magnitude. The enhancement at its maximum point 0.1 nm above the surface of a nanoshell is denoted $|E|_{\text{max}}(\lambda)$. For surface enhanced Raman scattering (SERS), the electromagnetic enhancement of the Raman cross section is approximately proportional to $|E|^4$ [14]. Averaging over the entire surface, denoted $\langle |E|^4 \rangle$, yields the efficacy of a given nanoparticle for SERS.
Chapter 2

Far Field Properties

Figure 2.1 shows the far field scattering, absorption, and extinction efficiencies of a small (Fig. 2.1(a)) and large (Fig. 2.1(b)) nanoshell with the same core to shell ratio.

Figure 2.1: Far field spectra, including $l = 1, 2,$ and 3 terms (dipole, quadrupole, and octopole, respectively), for nanoshells with (a) $r_1/r_2 = 8.0/9.5 \text{ nm}$ and (b) $r_1/r_2 = 80/95 \text{ nm}$. Individual $\sigma_+$ modes are indistinguishable on this scale. Note that in (a) the absorption efficiency overlaps the extinction efficiency for wavelengths above 150 nm.
There are two distinct phenomena leading to the features in the far-field spectra shown in Fig. 2.1: plasmon resonances due to the conduction electrons and geometric Mie cavity resonances. Plasmon resonances are collective oscillations of the conduction electrons in the metallic shell, discussed in section 1.2. Geometric Mie resonances occur when the physical size of the nanoparticle is on the same order as half the spatial wavelength of the incident light, i.e., when \( \lambda/n \approx 2 \times r_2 \) [3, 17, 31]. It is important to note that, while the \( l = 1, 2 \), and 3 terms suffice to describe the plasmon resonances, terms of higher order than those considered here contribute nontrivially in the geometric scattering regime.

Plasmon resonances in the absorption, scattering, and therefore extinction efficiencies are spectrally very similar in width and position (Fig. 2.1). The primary difference between the absorption and scattering efficiencies is their relative magnitude at each resonance and as a function of particle size and geometry. Small nanoshells (Fig. 2.1(a)) with a diameter of only a few percent of the spatial extent of the wavelength of incident light, known as the quasistatic limit, are primarily absorbers, while large nanoshells (Fig. 2.1(b)) couple strongly to light due to phase retardation and therefore predominantly scatter light. \( l > 1 \) modes couple weakly to light and hence predominately absorb even for large nanoshells (Fig. 2.1(b)) [14]. Because the intrinsic properties of nanoshell plasmons depend only on the core to shell ratio \( r_1/r_2 \), differences in the spectra of the small and large nanoshells shown in Fig. 2.1(a) and (b), respectively, are due entirely to extrinsic effects. This difference between extrinsic and extrinsic influences is clearly seen by examining the effect of removing the intrinsic material damping completely. Removing the intrinsic material damping can be accomplished by simply setting \( \Gamma = 0 \) in the Drude response (Eq. 1.2). For a small nanoshell, shown in Fig. 2.2(a), the resonance linewidth nearly vanishes when intrinsic material damping is turned off. In contrast, for the large nanoshell shown in Fig. 2.2(b), nearly the entire linewidth arises from extrinsic effects.
Figure 2.2: Comparison of the dipole extinction spectra with only extrinsic damping, and both intrinsic and extrinsic damping for nanoshells with (a) $r_1/r_2 = 8/9.5$ nm and (b) $r_1/r_2 = 80/95$ nm.

Figure 2.3 shows the dependence of the full width at half maximum (FWHM) for the symmetric dipole and quadrupole plasmon resonances in the extinction spectra and $\varepsilon''$ at the resonance wavelength on $\chi_\infty$ and $\Gamma$. $\chi_\infty$ causes dielectric screening of the surface charge, which reduces the restoring force experienced by the oscillating electrons, resulting in a redshift with increasing $\chi_\infty$. From the frequency dependence in the imaginary part of Eq. (1.3), it is apparent that this redshift increases $\varepsilon''$, thereby damping the resonance and increasing the FWHM as occurs in Fig. 2.3(a). In large particles, the FWHM is dominated by the extrinsic effects of damping due to emitting photons (scattering light) and phase retardation. Shifting the plasmon resonance to longer wavelengths makes the particle appear smaller relative to the spatial extent of the wavelength of incident light, decreasing the importance of phase retardation effects, and hence reducing the peak width as illustrated in Fig. 2.3(b). The weaker coupling of the quadrupole ($l = 2$) resonance to
the optical field, and hence lower sensitivity to extrinsic effects, results in a comparatively weaker dependence on $\chi_{\infty}$. Modifying $\Gamma$, unlike $\chi_{\infty}$, has the same affect on both small and large nanoshells, shown in Fig. 2.3 (c) and (d), because the resonant wavelength is only weakly dependent on the electronic damping and extrinsic effects therefore remain similar.

Figure 2.3: The full width at half maximum (FWHM) of the extinction efficiency peak corresponding to the symmetric dipole and quadrupole ($\sigma_-, l = 1$ and 2) plasmon resonances as a function of the background susceptibility $\chi_{\infty}$ and the reciprocal electronic relaxation time $\Gamma$. The geometry of the nanoshell in (a) and (c) is $r_1/r_2 = 8.0/9.5$ nm, while that of (b) and (d) is $r_1/r_2 = 80/95$ nm. The corresponding imaginary part of the shell dielectric function at the resonance wavelength is also indicated.
Chapter 3

Near Field Properties

Figure 3.1 displays the comparison between the maximum near field enhancement as a function of wavelength and the far-field extinction spectrum. The most striking differences are: a redshift in the peak wavelength, increased prominence of higher-order

![Figure 3.1: Maximum near field enhancement (|E| \text{max}(\lambda)) compared with the far field extinction spectra for both (a) r_1/r_2 = 8.0/9.5 nm and (b) r_1/r_2 = 80/95 nm nanoshells.](image)


Figure 3.2: Electric field intensity, at the resonance wavelength indicated, over a 200 x 200 nm region of space surrounding a nanoshell with $r_1/r_2 = 80/95$ nm. The polarization of the exciting plane wave is indicated to the left.

($l = 2, 3$) modes relative to the dipole ($l = 1$) mode, and a significant tail to the long wavelength side of the resonance. The higher-order modes are more prominent in the $|E|_{\text{max}}(\lambda)$ spectra because the field is concentrated into a smaller volume. The long wavelength tail is due to the nonresonant “lightning rod” effect, i.e. the quasistatic electric field conforming to the metallic boundary condition at the curved surface of the nanoshell [12]. Both the large and small nanoshell have a tail of similar magnitude because, at long wavelengths, both are small compared to the spatial variation of the field. The near field distribution corresponding to each of the larger nanoshell’s modes indicated in Fig. 3.1 is shown in Fig. 3.2. For the symmetric resonance, the dipole field enhancement is concentrated outside the nanoshell. This occurs because the charges on the inner and outer surfaces are in phase (see Fig. 1.3), resulting in a large overall dipole moment across the nanoshell. The antisymmetric resonance only has a large dipole moment across the shell, and the field is therefore concentrated inside the shell. This behavior is exhibited by
Figure 3.3: Full width at 3/4 maximum (FWTQM) and peak magnitude of the $\sigma_-, l = 1$ peaks in the maximum ($|E|_{\max}(\lambda)$) and surface average ($<|E|^4>$) enhancement spectra as a function of $\kappa_{\infty}$ and $\Gamma$. The nanoshell geometry in panels (a) and (c) is $r_1/r_2 = 8.0/9.5$ nm, while in (b) and (d) $r_1/r_2 = 80/95$ nm. Note that the $<|E|^4>$ curves are scaled by the factor indicated.

higher-order plasmon resonances as well. For the geometric cavity resonances, the field is distributed in a clear half-wave pattern along the direction of propagation, indicating the particle is acting as a resonant cavity.

Because the enhancement spectra do not return to the half-maximum value on the long wavelength side of the $\sigma_-, l = 1$ peak for most of the parameter space investigated, the near field peak widths are characterized by the full width at 3/4 maximum (FWTQM), shown in Fig. 3.3. These widths follow the same trends as the far field extinction spectra FWHMs shown in Fig. 2.3. The magnitude of the enhancement, also shown in Fig. 3.3, follows the opposite trend of the FWHMs, suggesting that the electromagnetic enhance-
ments are being distributed over a larger spectral range. Integrating the spectra over the FWTQM shows there is very small (less than a factor of 2) change in the overall strength of the electromagnetic field enhancement resonances as \( \chi_{\infty} \) and \( \Gamma \) are varied across the range of values examined here.
Chapter 4

Conclusions

Using a nanoshell geometry with a Drude dielectric function shell as a model system, I have examined the relationship between the dielectric function’s parameters and the optical properties of metallic nanoparticles. The spectral tunability of nanoshells allows for the separation of intrinsic and extrinsic influences on their optical response into core/shell \((r_1/r_2)\) ratio and absolute nanoparticle size effects. The FWHM of the far-field extinction spectra is linearly dependent on the reciprocal electron relaxation time \(\Gamma\), even for particles strongly influenced by phase retardation. The background susceptibility \(\chi_\infty\) of the material both affects the peak position and the FWHM of the extinction spectra. The wavelength dependence of the dielectric function leads to a change in resonance width due to the redshift of the plasmon resonance with increasing \(\chi_\infty\). For large particles, phase retardation and energy lost to scattering dominate the damping, leading to the opposite behavior. The redshift of the plasmon resonance decreases the importance of phase retardation, reducing the resonance linewidth. While the near field enhancement spectra follow trends similar to those of the far field extinction spectra, there are important differences between the near and far field spectra. The near field spectra is red-shifted with respect to the far field, higher order modes are relatively stronger, and a long wavelength
tail appears in the enhancement spectra. The spectral integral of the enhancement is only weakly dependent on both $\chi_{\infty}$ and $\Gamma$, showing that, in the near field, the resonance is being distributed over a larger spectral range.
Bibliography


