Lecture 11: Plasmonics

Thursday, October 18, 2017

Introduction: Free electrons in metals can couple strongly to light in certain geometries, those which effectively break the translational symmetry which exists in bulk metals. In such cases, we must solve Maxwell’s equations directly for the specific geometry. Local resonances whose origin is the collective motion of the electron gas, coupled strongly to light fields appear, the so-called surface plasmon. The synthesis and study of nanostructures which exhibit such resonant behavior, and exploiting these resonances in nano-structures for various applications is the burgeoning field known as plasmonics. The below excerpt from a recent paper in the journal *Science* shows a nano-metric ruler based on the extreme sensitivity of the plasmon resonances to changes in the relative position of several nano-sized noble metal “antennas”, which could be utilized in a nano-metric sensor (images from the journal *Science*).

![Figure 1: A plasmonic sensor, based on the relative position of two “quadrapole” plasmonic nanostructures (shown in yellow and green in the inset) with a “dipole” plasmonic nanostructure (shown in red in the inset). The change in the measured and theoretically predicted absorption spectra as a function of the relative position of these antenna is shown for one symmetric and two non-symmetric arrangements.](image)

Frequency dependent dielectric constant: We often assume the dielectric properties of polarizable media are constants, which for fields of monochromatic nature, is an accurate description. However, it is well-known that the permittivity and permeability of materials varies significantly with frequency. The great utility of plane wave analysis is that we can extract solutions to Maxwell’s equations for these simple objects, and by superposition construct more complex functions. However, the relative amplitudes and phases of these plane-wave components will be of importance. These variations in amplitude, phase, and speed of propagation of plane waves of varying frequencies are known as material dispersion.

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We may assume the polarizability of materials originates from induced dipoles formed by the Coulomb force of an applied electric field on the bound charges resident in polarizable media. An imposed electric field distorts these charges as shown in figure 2:

Figure 2: (left): charge distortion $\delta r$ in ponderable media upon application of an external field $E$. (center): Force vs radial distance of Coulomb force on charges in ponderable media. (right): Damped harmonic oscillator model of the electron motion in ponderable media, $\gamma$ is defined as the damping divided by $m$, and $\omega_p^2 = k/m$.

For a small range of $\delta r$, the Coulomb force can be assumed to be linear and follow Hooke’s law: $F_c = -k_{eff}x$, thus we can write an equation of motion for the bound electron:

$$m\ddot{x} + m\gamma\dot{x} + m\omega_p^2 x = -eE$$

From which, if we assume time-harmonic dependence of the electric field, the resulting displacement $\delta r \equiv x$ will also be time-harmonic:

$$x = \frac{-e}{m\omega_p^2 - \omega^2 - i\gamma\omega} E$$

As the dipole moment is $p = -ex$, we need simply to include all N dipoles per unit volume to get the polarization field:

$$D = \epsilon E = E + 4\pi N e^2 \frac{E}{m\omega_p^2 - \omega^2 - i\gamma\omega}$$

from which we can write:

$$\epsilon(\omega) = 1 + \frac{4\pi N e^2}{m} \frac{1}{\omega_p^2 - \omega^2 - i\gamma\omega} = 1 + \frac{\omega_p^2}{\omega_p^2 - \omega^2 - i\gamma\omega} \rightarrow \omega_p^2 = \frac{4\pi N e^2}{m}$$

Where we have defined the plasma frequency, $\omega_p$, which is essentially the frequency after which the electrons can no longer completely screen the externally applied field. In metals, the restoring force is extremely weak, and the term $\omega_p^2$ can be dropped at frequencies of interest, equivalent to “cutting the spring” in the damped oscillator model, giving:

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} = 1 - \frac{\omega_p^2}{\omega(\omega + i\gamma)} \approx 1 - \frac{\omega_p^2}{\omega^2} \quad \text{for small damping and high frequencies}$$

The above expressions do not take into account the possibility that the polarization may be greater than unity at infinite frequency, which is usually accounted for by inserting $\epsilon_\infty$ into the above equations, and defining a new plasma frequency $\bar{\omega}_p = \omega_p/\sqrt{\epsilon_\infty}$:

$$\epsilon(\omega) = \epsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} \rightarrow \frac{\epsilon(\omega)}{\epsilon_\infty} = 1 - \frac{\bar{\omega}_p^2}{\bar{\omega}(\bar{\omega} + i\gamma)} \approx 1 - \frac{\bar{\omega}_p^2}{\bar{\omega}^2} \quad \text{(final form for small damping and high frequencies)}$$
The above expressions tell us that the dielectric constant becomes negative for frequencies below $\bar{\omega}_p$, which means the refractive index becomes imaginary:

$$n = \sqrt{\varepsilon} \quad \rightarrow \quad n \text{ is a complex number for } -\text{ve } \varepsilon(\omega)$$

thus for plane waves of the form $E(x, t) \propto e^{i(kx-\omega t)}$, where $k = n2\pi/\lambda$, this will result in exponential decay:

$$E(x, t) \propto e^{-|\sqrt{\varepsilon(\omega)}| \frac{2\pi}{\lambda} x} e^{-i\omega t}$$

As conservation of energy requires that $T + R + A = 1$, where $T$ is the transmission, $R$ the reflection and $A$ the absorption, and for weak damping $A$ can be neglected, if the transmission $T$ is small for frequencies below $\omega_p$, the reflectivity must be high. Thus, as illustrated below, the metals described by the above analysis are highly reflective for electromagnetic radiation with frequencies below the plasma frequency:

![Reflectivity graph](image)

Figure 3: Reflectivity for a metal described by plasma frequency $\omega_p$, showing that waves below the plasma frequency cannot propagate in the metal and are reflected with near 100% efficiency.

**Plasmons**: A collective oscillation of electrons may be excited in a metal, which may be assumed to be a plasma, i.e. a “gas” of positive and negative charges, which is overall neutral but the constituent charges can still be influenced by applied fields. If an electric field is applied to a plasma, charges may move and an excitation called a plasmon can occur. As seen in the figure below, such an excitation is not an equilibrium state, and has some restoring force which drives the oscillation. These collective oscillations of the electron gas are termed plasmons. A close look at

![Plasmon diagram](image)

Figure 4: (left): An electron gas surrounding the positive ions in a metal can be considered a plasma, a gas of charged particles which is overall electrically neutral. (right): A collective oscillation in a plasma is termed a plasmon.
the figure shows that the plasmon is describable by a plane wave, with an associated wavelength $\lambda_p$ and wavenumber $k_p$. Thus we may solve a wave-equation for the propagation of the plasmon, assuming a lossless dielectric constant as derived above:

$$\frac{\partial^2 D}{\partial t^2} = c^2 \nabla^2 E \quad \rightarrow \quad \varepsilon(\omega) \omega^2 E = c^2 k^2 E \quad \rightarrow \quad \varepsilon_{\infty}(1 - \frac{\omega_p^2}{\omega^2})\omega^2 = c^2 k^2 \quad \rightarrow \quad \omega^2 = \omega_p^2 + \frac{k^2 c^2}{\varepsilon_{\infty}}$$

The last form is the dispersion relation for the plasmon in bulk metal, that is the *volume* plasmon, plotted below:

![Plasmon Dispersion Relation](image)

**Surface Plasmon**: Note the two curves shown above don’t cross. That is, energy and momentum cannot be conserved in the interaction of a photon with the volume plasmon. Thus, to excite the plasmon with light, we must introduce some coupling mechanism, which can be used to make up the momentum mismatch. This can be done by introducing geometrical effects. The common feature is that all the mechanisms involve breaking the translational symmetry inherent in the above dispersion relations by matching the electromagnetic wave to the plasmon at a surface. At a surface, we can match the energy momentum relation of the plasmon to that of light; and the collective oscillation of the electron gas, coupled strongly to an electromagnetic wave, is termed the *surface plasmon*.

The surface plasmon can be excited by prism coupling, grating coupling, or introducing any nano-structure which produces sub-wavelength corrugation. The field of plasmonics is the study of the resulting surface plasmons and controlling the flow of electromagnetic energy near metallic surfaces and nano-structures. Let us derive a dispersion relation for the surface plasmon by solving Maxwell’s equations for the geometry shown below:

![Surface Plasmon Dispersion Relation](image)

**Figure 5**: The dispersion relation for the volume plasmon, compared to the dispersion relation for light.

**Figure 6**: Excitation of the surface plasmon in a thin-metal film deposited on the surface of a prism.
We can assume we have a plane wave incident on a hemispherical prism, as shown in the figure. The fields have the form: 

\[ E_i = E_{oi} e^{i(k_{yi} y \pm k_{zi} z - \omega t)} \]  

and 

\[ H_i = H_{oi} e^{i(k_{yi} y \pm k_{zi} z - \omega t)} \]

with 

\[ H_{oi} = H_{xi} \hat{x} \] 

and 

\[ E_{oi} = E_{yi} \hat{y} + E_{zi} \hat{z} \]

\( i = 1, 2 \), corresponding to \( \varepsilon_1 \) and \( \varepsilon_2 \). Putting these into Maxwell’s vector equations:

\[ \nabla \times E = \frac{1}{c} \frac{\partial B}{\partial t} \quad \text{and} \quad \nabla \times H = \frac{1}{c} \frac{\partial D}{\partial t} \]

and assuming time-harmonic fields yields:

\[ \nabla \times E = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ \partial_x & \partial_y & \partial_z \\ 0 & E_{yi} & E_{zi} \end{vmatrix} = (ik_{yi} E_{zi} \mp ik_{zi} E_{yi}) \hat{i} - \frac{1}{c} \frac{\partial B}{\partial t} = \frac{i}{c} \omega H_{xi} \hat{i} \]  

(1)

\[ \nabla \times H = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ \partial_x & \partial_y & \partial_z \\ H_{xi} & 0 & 0 \end{vmatrix} = (\pm ik_{zi} H_{xi}) \hat{j} - (ik_{yi} H_{xi}) \hat{k} = \frac{1}{c} \frac{\partial D}{\partial t} = -i \varepsilon_i \frac{\omega}{c} (E_{yi} \hat{j} + E_{zi} \hat{k}) \] 

(2)

Equating the vector components yields the system of equations:

\[ i \frac{\omega}{c} H_{xi} = ik_{yi} E_{zi} \mp ik_{zi} E_{yi} \quad \text{for} \quad i = 1, 2 \]  

(3)

\[ \pm ik_{zi} H_{xi} = -i \varepsilon_i \frac{\omega}{c} E_{yi} \quad \text{for} \quad i = 1, 2 \]  

(4)

\[ -ik_{yi} H_{xi} = -i \varepsilon_i \frac{\omega}{c} E_{zi} \]  

(5)

From the above equations and the boundary conditions \( E_{1t} = E_{2t}, \ D_{1n} = D_{2n} \) and \( H_{1t} = H_{2t} \), we can show:

\[ \frac{k_{z2}}{\varepsilon_2} + \frac{k_{z1}}{\varepsilon_1} = 0 \quad \text{and} \quad \varepsilon_i \frac{\omega^2}{c^2} = k_{zi}^2 + k_{yi}^2 \quad (i = 1, 2) \]

giving the dispersion relation: 

\[ k_y = k_{sp} = \frac{\omega}{c} \sqrt{\frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2}} \]

Inserting the above form(s) for \( \varepsilon(\omega) \) into the expression for \( k_{sp} \) yields:

\[ k_{sp} = \frac{\omega}{c} \sqrt{\frac{\varepsilon_1 (\varepsilon_{2b} - \omega_p^2)}{\varepsilon_1 + \varepsilon_{2b} - \omega_p^2}} \]

\( \omega \) \( \varepsilon_{2b} \) is the polarizability of the metal far beyond the plasma frequency. With the proper choice of units, \( \varepsilon_{2b} \) and \( \varepsilon_1 \) can be taken as unity, which gives the simplified form shown above, and plotted below:

Figure 7: Dispersion relation of the surface plasmon in a thin-metal film on the surface of a prism.
Surface plasmons of small particles: While the surface plasmon can be excited using a prism at a semi-infinite interface between a metal and a dielectric, it is also possible to excite such oscillations on curved surfaces, or surfaces with corrugation on the order or smaller than the wavelength of light. The classic treatment of the modes excited by light at the surface of a spherical particle due to Mie\(^2\) is an analytical dissertation on this topic. It begins with the scattering geometry shown below:

![Figure 8: Plane wave incident on a small sphere of dielectric constant \(\varepsilon^II\) from a medium of dielectric constant \(\varepsilon^I\).](image)

The analysis is sketched as follows: first, incident field is taken to be \(\mathbf{E}^i = e^{ik^Iz}\mathbf{x}\) and \(\mathbf{H}^i = \frac{ik^I}{k_2}e^{ik^Iz}\mathbf{y}\) and considered to be time-harmonic, thus the vector Maxwell’s equations can be written as:

\[
\nabla \times \mathbf{H} = -k_1 \mathbf{E} \quad \text{where} \quad k_1 = \frac{i\omega}{c} \left( \varepsilon + i\frac{4\pi\sigma}{\omega} \right)
\]

and

\[
\nabla \times \mathbf{E} = k_2 \mathbf{H} \quad \text{where} \quad k_2 = \frac{i\omega}{c}
\]

The boundary conditions are: \(H^I_t = H^II_t\), and \(E^I_t = E^II_t\) at \(r = a\), the radius of the sphere. Writing out the first set of Maxwell’s equations for the curl of \(\mathbf{H}\) gives expressions for the vector components of \(\mathbf{E}\):

\[
-k_1 E_r = \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( r H_{\phi} \sin \theta \right) - \frac{(r H_{\theta})}{\partial \theta}
\]

\[
-k_1 E_\theta = \frac{1}{r \sin \theta} \left[ \frac{\partial H_r}{\partial \phi} - \frac{\partial (r H_\phi \sin \theta)}{\partial r} \right]
\]

\[
-k_1 E_\phi = \frac{1}{r} \left[ \frac{\partial (r H_\theta)}{\partial r} - \frac{\partial H_r}{\partial \theta} \right]
\]

and similar equations for \(\mathbf{H}\). You may assume the solutions come in two forms (akin to TE and TM):

\((^* \mathbf{E}, ^* \mathbf{H})\) and \((^m \mathbf{E}, ^m \mathbf{H})\)

transversality of the solutions requires that $E_r = E_r$, $H_r = 0$ and $mE_r = 0$, $mH_r = H_r$. Thus, we can simplify the above expressions to come up with the following set of equations:

\[-k_1E_r = \frac{1}{r^2 \sin \theta} \left[ \frac{\partial}{\partial \theta} (r^H \phi \sin \theta) - \frac{\partial}{\partial \phi} (r^H \phi) \right]\]  \hspace{1cm} (9)

\[\left( \frac{\partial^2}{\partial r^2} + k^2 \right) \left( r^H \phi \right) = -\frac{k_1}{\sin \theta} \frac{\partial E_r}{\partial \phi} \]  \hspace{1cm} (10)

\[\left( \frac{\partial^2}{\partial r^2} + k^2 \right) \left( r^H \phi \right) = k_1 \frac{\partial E_r}{\partial \phi} \]  \hspace{1cm} (11)

\[\frac{1}{k_1^2 r^2 \sin \theta} \frac{\partial}{\partial r} \left[ \frac{\partial}{\partial \theta} (r \sin \theta H_\theta) + \frac{\partial (r^H \phi)}{\partial \phi} \right] = 0 \]  \hspace{1cm} (12)

where the last equation comes from $\nabla \cdot \mathbf{E} = 0$. To solve these equations, Mie used potential theory, and introduced the Debye potentials $\varepsilon \pi$ and $m \pi$ which can be found by the method of separation of variables:

\[m \varepsilon \pi = R(r) \Theta(\theta) \Phi(\phi)\]

By introducing these potentials, the above equations are separable, and we obtain ordinary differential equations of the form of Bessel’s equation, Legendre’s equation and the harmonic equation:

\[\frac{d^2 (r R(r))}{dr^2} + \left(k^2 - \frac{\alpha}{r^2} \right) r R(r) = 0 \]  \hspace{1cm} (13)

\[\frac{1}{\sin \theta} \frac{d}{d \theta} \left( \sin \theta \frac{d \Theta(\theta)}{d \theta} \right) + \left( \alpha - \frac{\beta}{\sin^2 \theta} \right) \Theta(\theta) = 0 \]  \hspace{1cm} (14)

\[\frac{d^2 \Phi(\phi)}{d \phi^2} + \beta \Phi(\phi) = 0 \]  \hspace{1cm} (15)

with well known solutions:

\[\Phi(\phi) = a_m \cos(m \phi) + b_m \sin(m \phi) \]  \hspace{1cm} (16)

\[\Theta(\theta) = P_l^{(m)}(\xi) = P_l^{(m)}(\cos \theta) \quad m = -l, -l + 1, ..., l - 1, l \]  \hspace{1cm} (17)

\[R(r) = \frac{1}{r} \zeta_l^{(1)}(kr) \quad \text{where} \quad \zeta_l^{(1)}(\rho) = \sqrt{\frac{\pi \rho}{2}} H_{l+\frac{1}{2}}^{(1)}(\rho) \]  \hspace{1cm} (18)

where $H_{l+\frac{1}{2}}^{(1)}(\rho)$ is the Hankel function of the first kind. The potentials can thus be assembled and the field obtained according to the generating equations:

\[E_r = \varepsilon E_r + mE_r = \frac{\partial^2 (r \varepsilon \pi)}{\partial r^2} + k^2 r \varepsilon \pi \]  \hspace{1cm} (19)

\[\varepsilon E_\theta + mE_\theta = \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial (r m \varepsilon \pi)}{\partial \theta} \right) \]  \hspace{1cm} (20)

\[E_\phi = \varepsilon E_\phi + mE_\phi = \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi} \left( r \sin \theta \frac{\partial (r m \varepsilon \pi)}{\partial \theta} \right) \]  \hspace{1cm} (21)

With the solutions (16)-(18), we can construct $\varepsilon \pi$ and $m \pi$ and with the assistance of (19)-(21) calculate the fields (shown here are the electric fields only):

\[E_r^{(s)} = \frac{1}{(k^2 r)^2} \frac{\cos \phi}{\sin \theta} \sum_{l=1}^{\infty} \frac{l(l+1)}{r} \varepsilon B_l \zeta_l^{(1)}(k r) P_l^{(1)}(\cos \theta) \]  \hspace{1cm} (22)

\[E_\theta^{(s)} = -\frac{1}{k^2 r} \cos \phi \sum_{l=1}^{\infty} \left[ \varepsilon B_l \zeta_l^{(1)}(k r) P_l^{(1)}(\cos \theta) \sin \theta - i m B_l \zeta_l^{(1)}(k r) P_l^{(1)}(\cos \theta) \right] \]  \hspace{1cm} (23)

\[E_\phi^{(s)} = -\frac{1}{k^2 r} \sin \phi \sum_{l=1}^{\infty} \left[ \varepsilon B_l \zeta_l^{(1)}(k r) P_l^{(1)}(\cos \theta) \sin \theta \right] \]  \hspace{1cm} (24)
Thus we see the various combinations of special functions found in (22)-(24) are weighted by the coefficients \( e^B_l \) and \( m^B_l \), similar to a multi-pole expansion. Essentially, the problem of Mie theory is to map the amplitude of plane waves onto a sphere, similar to scattering theory encountered in the study of quantum mechanics. This is sometimes referred to as a partial wave expansion. The \( \epsilon^{(m)}B_l \) are termed the partial-wave amplitudes for the \( l^{th} \) partial wave. In many circumstances, one or a few terms in this expansion can reproduce all the observed properties. Each term has unique symmetry, and it is often useful to examine these waves. The first two-partial waves and the electric and magnetic lines of force described by the respective terms in (22)-(24) are shown in the figure below:

\[
\epsilon^{B_1} = \frac{i q}{n^2 + 2} = i (\frac{2 \pi a}{\lambda})^3 \frac{n^2 - 1}{n^2 + 2}, \quad \text{where} \quad n^2 = (\frac{k^{II}}{k^I})^2 = \frac{\epsilon^{II}}{\epsilon^I} + \frac{4 \pi \sigma}{\omega \epsilon^I}
\]

thus for high \( \omega \) or low \( \sigma \), \( \epsilon^{B_1} = i \left( \frac{2 \pi a}{\lambda} \right)^3 \frac{\epsilon^{II} - \epsilon^I}{\epsilon^{II} + 2 \epsilon^I} \rightarrow \text{resonance} @ |\epsilon^{II} + 2 \epsilon^I| = 0 \]

We see that the amplitude of the first partial wave can become very large for a specific frequency which makes \( \epsilon^{II}(\omega) = -2 \epsilon^I \), this is the plasmon frequency. As seen in the figure below, this frequency depends on the size of the particle due to the so-called Fermi-damping, which modifies the intrinsic material damping in the Drude form for \( \epsilon^{II}(\omega) \) by adding an additional term which is size-dependent: \( \epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i \gamma \omega} \quad \text{where} \quad \gamma = \gamma_{\text{bulk}} + \frac{\nu_F}{a}. \)

![Figure 9: First two parial waves and the lines of electric and magnetic force. Nodes are represented by “o”.

If we introduce the scaling parameter \( q = 2 \pi \frac{a}{\lambda} \), and if \( q \ll 1 \), we may assume only the first partial wave is non-zero:

\[
\epsilon^{B_1} = \frac{3}{n^2 + 2} = \left( \frac{2 \pi a}{\lambda} \right)^3 \frac{n^2 - 1}{n^2 + 2}, \quad \text{where} \quad n^2 = \left( \frac{k^{II}}{k^I} \right)^2 = \frac{\epsilon^{II}}{\epsilon^I} + \frac{4 \pi \sigma}{\omega \epsilon^I}
\]

Figure 10: Energy-losses due to electrons with finite mean-free path \( \lambda_{\text{mfp}} \) and velocities \( v_F \) scattering into surface states increase as the particle size \( a \) decreases, the so-called Fermi-damping.