General Properties of Local Plasmons in Metal Nanostructures

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Under the quasistatic approximation, the characteristics of a local plasmon resonance of a metal nanostructure exhibit several general properties. The resonance frequency depends on the fraction of plasmon energy residing in the metal through the real dielectric function of the metal. For a given resonant frequency, the Q factor of the resonance is determined only by the complex dielectric function of the metal material, independent of the nanostructure form or the dielectric environment. A simple result describing the effect of optical gain on the Q factor is also obtained.

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Plasmon resonance in nanoscale metal structures has been a focus of intensive research activity in recent years [1–4]. The increasing interests in local plasmons stem both from the existence of a large variety of metal nanostructures, either from chemical synthesis [5–8] or nanofabrication [9–11], and their unique properties. It has been shown that the metal structures can dramatically enhance the local electrical field by concentrating electromagnetic energies into subwavelength volumes. This could lead to a wide spectrum of applications, ranging from single molecule Raman scattering [12,13] to sub-diffraction limit imaging [14,15] to efficient optical mixing [11,16]. Many ingenious designs of metal nanostructures have been proposed to achieve these goals. In order to gain further insight on local plasmon resonances, one would like to know more about their general behavior without referring to the specific nanostructures.

In this Letter, we explore properties of local plasmon resonance common to all metal nanostructures by examining energy relations involving such resonance. As is true for many physical processes, an energy perspective frequently yields simple but general and useful results. We show that in the quasistatic limit, the energy of the local plasmon field within the metal part of a nanostructure is always larger than that in the surrounding media. The ratio of the two has a simple exclusive dependence on the real dielectric functions of the metals at the resonant frequency. As such, the plasmon resonance frequency of a nanostructure, being the implicit variable in the metal dielectric functions, can be tuned through varying this energy ratio. We further show that for a given resonance frequency, the quality factor (Q factor) of the plasmon resonance should depend solely on the complex dielectric function of the material, independent of the geometry of the nanostructure. The energy relation also allows us to set a simple criterion necessary for optical gain in the dielectric medium to compensate the loss in the metal part of a nanostructure.

In analogy to the optical resonances in microcavities, local plasmons can be regarded as local modes originating from coupling between the electromagnetic field and excitation in metal. More formally, they are localized eigenmodes of the Maxwell equations and their resonant width is characterized by the associated Q factor. We consider here a metal nanostructure of arbitrary form. The field distribution spreads over metal and dielectric parts, both of which may consist of multiple components and compositions. On the nanoscale, the optical wave retardation effect is small and the problem can be treated with quasistatic approximation. It amounts to solving Maxwell equations in the lowest order with the time-dependent terms in the equations taken as perturbation. In the formalism, the Maxwell equations are written as

$$\vec{\nabla}\cdot\vec{B}=0, \qquad \vec{\nabla}\times\vec{B}=(\eta/c)(\partial\vec{D}/\partial t),$$
$$\vec{\nabla}\cdot\vec{D}=0, \qquad \vec{\nabla}\times\vec{E}=-(\eta/c)(\partial\vec{B}/\partial t),$$

with $\vec{D}=\varepsilon\vec{E}$, $\varepsilon=\varepsilon'+i\varepsilon''$ and the perturbative solution has the form

$$\vec{E}=\vec{E}^{(0)}+\eta\vec{E}^{(1)}+O(\eta^2);$$
$$\vec{B}=\vec{B}^{(0)}+\eta\vec{B}^{(1)}+O(\eta^2).$$

Here, η is an expansion parameter introduced to keep track of the orders of perturbation and is set to 1 in the end result. The optical response is characterized solely by the dielectric constant ε that is position dependent and the magnetic permittivity is taken to be 1. In the lowest order, we have only $\vec{E}^{(0)}\neq\vec{0}$, i.e., the local plasmon resonance is purely electric in the quasistatic limit. A criterion for the validity of quasistatic approximation is that the ratio of nanostructure dimension L to reduced wavelength λ is much smaller than 1 ($L/\lambda=kL\ll 1$). For larger nanostructures with $L/\lambda\sim 1$, the results from quasistatic approximation can still serve as guidance.

We examine here general energy relations of local plasmon modes in the quasistatic limit. We are interested in the frequency region below the bulk plasma frequency of the low-loss metal so that $\varepsilon_m'<0$, but $\frac{d(\omega\varepsilon_m')}{d\omega}>0$ and $\varepsilon_m''\ll|\varepsilon_m'|$. We first show that time-averaged electromagnetic (em) energy, $\bar{U}_m$, residing in the metal part is always larger than time-averaged em energy, $\bar{U}_d$, contained in the dielec-

tric part of a nanostructure system, with $\bar{U}_m$ and $\bar{U}_d$ having the expressions [17]

$$\bar{U}_m = \frac{1}{8\pi}\int_{\Omega_{\text{metal}}} \frac{d(\omega\varepsilon'_m)}{d\omega}\overline{E^2}dV;$$
$$\bar{U}_d = \frac{1}{8\pi}\int_{\Omega_{\text{dielectric}}} \varepsilon_d\overline{E^2}dV. \quad (1)$$

Here, for simplicity, the dielectric medium is assumed to be lossless and have negligible dispersion, and Ω_{metal} and $\Omega_{\text{dielectric}}$ denote the volumes occupied by the metal and the dielectric medium, respectively.

For the proof, we notice that for any local field in the quasistatic limit, $\vec{\nabla}\times\vec{E}=0$ and $\vec{E}\equiv-\vec{\nabla}\Phi$, we have

$$\int_\Omega \varepsilon\vec{E}\cdot\vec{E}dV = \int_\Omega \vec{E}\cdot\vec{D}dV = -\int_\Omega \vec{\nabla}\Phi\cdot\vec{D}dV$$
$$= -\int_\Omega [\vec{\nabla}\cdot(\Phi\vec{D}) - \Phi(\vec{\nabla}\cdot\vec{D})]dV$$
$$= -\oint_{S_\Omega} \Phi(\vec{D}\cdot\vec{n})ds = 0,$$

where Ω refers to a large volume enclosing the nanostructure. Its surface S_Ω is far away from the local resonant field range of the nanostructure, so that in the quasistatic limit, we have $D=0$ at S_Ω. The equation holds true in general for any local modes within quasistatic approximation. One observes that for a nontrivial solution of the electric field to exist, ε cannot be positive everywhere. This points to the fact that metal or other materials with negative dielectric constants are required for nanostructure to have local resonance (with localization much smaller than wavelength). With Ω divided into Ω_{metal} and $\Omega_{\text{dielectric}}$, we have, from $\int_\Omega \vec{E}\cdot\vec{D}dV=0$, the identity

$$\int_{\Omega_{\text{dielectric}}} \varepsilon_d\overline{E^2}dV = \int_{\Omega_{\text{metal}}} -\varepsilon'_m\overline{E^2}dV. \quad (2)$$

For local plasmons in low-loss metal nanostructures, the resonance frequencies lie in the visible or near infrared range, away from any absorption peaks. In this case, we can show from the analytical property of a dielectric function, $\varepsilon'(\omega) = 1+\frac{2}{\pi}\mathrm{P}\int_0^\infty \frac{x\varepsilon''(x)}{x^2-\omega^2}dx$, that $\frac{d(\omega\cdot\varepsilon'_m)}{d\omega} = -\varepsilon'_m + 2 + \frac{2}{\pi}\mathrm{P}\int_0^\infty \frac{2x^3\varepsilon''_m}{(x^2-\omega^2)^2}dx > -\varepsilon'_m$. It then follows from Eqs. (1) and (2) that

$$\frac{\bar{U}_m}{\bar{U}_d} = \frac{\int_{\Omega_{\text{metal}}}\frac{d(\omega\varepsilon'_m)}{d\omega}\overline{E^2}dV}{\int_{\Omega_{\text{metal}}}(-\varepsilon'_m)\overline{E^2}dV} \geq 1.$$

If the nanostructure contains only one type of metal, ε_m can be taken out of the integration, which then yields

$$\bar{U}_m/\bar{U}_d = \frac{d(\omega\varepsilon'_m)}{d\omega}\Big/(-\varepsilon'_m) \geq 1. \quad (3)$$

The ratio is determined solely by the metal dielectric constant around the plasmon resonance frequency and remains the same for nanostructures of different shape or form with a given resonance frequency. We present in Fig. 1 the energy ratios versus plasmon frequency for nanostructures made of silver and gold [18], the two mostly commonly used materials, and of an "ideal" metal described by the Drude model.

This general conclusion on energy ratio is rather unexpected and may seem counterintuitive in certain cases. For instance, consider the symmetric mode of a metal nanoshell [Fig. 2(b)]. One might think that decreasing of the shell thickness would decrease the em energy residing in the metal and eventually make the conclusion invalid. This does not happen because the reduced metal thickness redshifts the plasmon resonant frequency and causes $\frac{d(\omega(\varepsilon'_m)}{d\omega}$ to increase and compensate the volume reduction in the expression of $\bar{U}_m$. This keeps $\bar{U}_m/\bar{U}_d$ larger than 1 although the exact value may vary.

The simple result on local-field energy distribution of Eq. (3), or the closely related field intensity distribution in Eq. (2), can help us understand a wealth of plasmon behavior. We consider first variation of the plasmon resonance frequency with the nanostructure design. This is most apparent through Eq. (2), which can be recast into the form

$$-\varepsilon'_m = \int_{\Omega_{\text{dielectric}}} \varepsilon_d\overline{E^2}dV \Big/ \int_{\Omega_{\text{metal}}} \overline{E^2}dV. \quad (4)$$

For metals, $-\varepsilon_m$ increases monotonically with decrease of frequency below the bulk plasmon frequency (inset of Fig. 1). In the design searching for a lower plasmon resonance frequency in a nanostructure, for instance, we must have a larger $-\varepsilon_m$, and following Eq. (4), we must increase

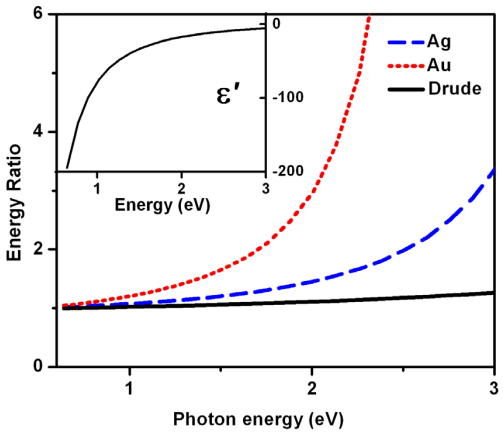

FIG. 1 (color online). Plots of the ratios of plasmon energies in the metal nanostructure to that in the surrounding dielectric medium versus plasmon resonance frequency for metal materials of gold (dashed line), silver (dotted line), and ideal Drude free-electron metal (solid line). Results depend only on the dielectric functions of the metals but not on the specific nanostructure. Dielectric constants for gold and silver used in the calculation were obtained from Ref. [18]. The bulk plasmon frequency of the Drude metal is chosen to be at 9 eV to facilitate comparison with silver and gold. The inset shows qualitatively the frequency dependence of the real dielectric constant of a typical metal below its bulk plasmon frequency.

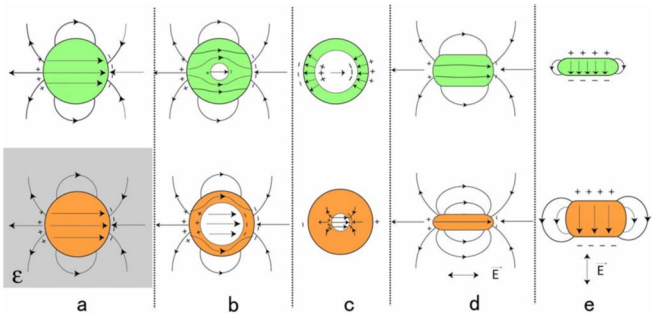

FIG. 2 (color online). Examples of field distribution affecting the plasmon resonance frequency of a metal nanostructure. (a) Metal spheres imbedded in different dielectric media, (b) metal nanoshells of different thicknesses with symmetric plasmon mode, (c) metal nanoshells of different thicknesses with antisymmetric plasmon mode, (d) metal nanorods of different aspect ratios with field polarization parallel to the rod, and (e) metal nanorods of different aspect ratios with field polarization perpendicular to the rod.

the ratio on the right-hand side. Figure 2 provides a few specific examples to achieve this: In Fig. 2(a), we have a metal sphere in different dielectric media. The field distributions are the same in the two cases, and the ratio gets larger for higher ε_d. In Fig. 2(b), the symmetric mode of a metal nanoshell has a field pattern relatively insensitive to the shell thickness. Thinning the shell then decreases the metal volume and increases the ratio. The antisymmetric mode of the nanoshell described in Fig. 2(c), however, has the opposite behavior. The field is drawn into the metal by the opposite charges at two close surfaces in a thin shell. It becomes less concentrated in the metal (and has a larger ratio) when the shell thickness increases. Figure 2(d) shows that a larger aspect ratio of a metal nanorod has more field lines spread out in the dielectric medium for filed polarization parallel to the rod, and hence a larger ratio. For polarization perpendicular to the nanorod, displayed in Fig. 2(e), the behavior is opposite; a smaller aspect ratio now has a larger percentage of fringe field lines spread out into the dielectric medium. For all these cases, the prediction of a red-shift resulting from the increased ratio in Eq. (4) is consistent with the more elaborated calculations and experimental observations on metal nanospheres [19], nanoshells [20–22], and nanorods [23].

Aside from the resonance frequency, the other important parameter for plasmon resonance is the quality factor Q. A higher Q factor representing a sharper resonance is often desirable as it leads to stronger local-field enhancement. With loss occurring only in the metal part of the nanostructure, the Q factor has the expression [24]:

$$Q \equiv \frac{\omega \bar{U}_{\text{total}}}{d\bar{U}_{\text{total}}/dt} = \frac{\int_{\Omega_{\text{metal}}} \frac{d(\omega\varepsilon'_m)}{d\omega} \overline{E^2} dV + \int_{\Omega_{\text{dielectric}}} \varepsilon_d \overline{E^2} dV}{2\int_{\Omega_{\text{metal}}} \varepsilon''_m \overline{E^2} dV} = \frac{\omega \frac{d\varepsilon'_m}{d\omega}}{2\varepsilon''_m}. \quad (5)$$

Equation (5) shows surprisingly that the Q factor of the plasmon resonance also depends only on the dielectric function of the metal at the given plasmon frequency but not on the geometric form and shape of the nanostructure and the dielectric media (assumed to be dispersionless and lossless). This means that there is not much one can do to improve the sharpness of the plasmon resonance once the metal material and resonance frequency are chosen. For example, one can design different gold nanostructures like nanorods or nanoshells to have the same plasmon frequency, but one would find that all the plasmon resonances have the same sharpness. In Fig. 3, we show the Q factor versus plasmon frequency for nanostructures of gold and silver. The result should be useful as a guide in the nanostructure design aiming for a desirable plasmon resonance. We note that we have neglected loss from radiation and surface imperfection. Such losses effectively increase the loss coefficient ε''_m, and may make Q factor smaller and vary for different nanostructures. In the quasistatic limit, the radiation loss is small, but it can grow rapidly as the nanostructure size increases and lead to broader resonance. The surface imperfection loss has been found to be small in high quality metal nanostructures [23].

We can use analytically solvable cases to confirm our general results. Consider, for example, a metal nanoellipsoid in a uniform dielectric medium. The induced dipole moment on the ellipsoid by an external field E^{ext} is [17]

$$p_i = \tfrac{1}{3} abc(\varepsilon^m - \varepsilon^d) E_i^{\text{ext}} / [\varepsilon^d + (\varepsilon^m - \varepsilon^d) n_i],$$

where a, b, c are the three semiaxis lengths, subscript i denotes the ith principle axis, and n_i are real numbers depending on the ellipsoid geometry. The plasma resonance is characterized by the resonant denominator with the resonant frequency ω_0 and the half-width $\Delta\omega$ deduced from [24]

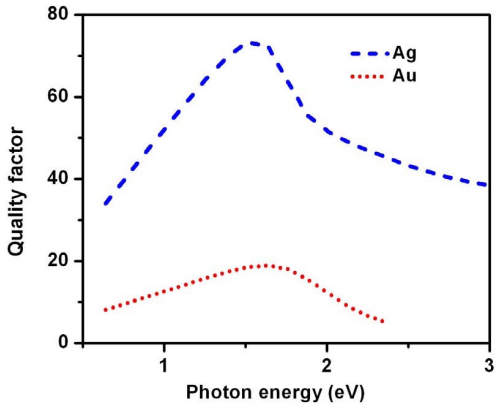

FIG. 3 (color online). Quality factor versus resonance frequency for plasmon resonances in metal nanostructures. Results for gold (dashed line) and silver (dotted line) are displayed and they are independent of the shape and form of nanostructures.

$$\begin{aligned} &\mathrm{Re}[\varepsilon_d + (\varepsilon_m(\omega_0) - \varepsilon_d)n_i] = 0, \\ &\mathrm{Re}[\varepsilon_d + (\varepsilon_m(\omega_0 + \Delta\omega) - \varepsilon_d)n_i = \mathrm{Im}[\varepsilon_m(\omega_0)n_i], \end{aligned} \tag{6}$$

where $\varepsilon_m'' \ll \varepsilon_m'$ and ε_d is real. It is then straightforward to show that $Q = \omega_0/2\Delta\omega$ from Eq. (6) has the same expression as the general one in Eq. (5).

Finally, we investigate the effect of optical gain in the dielectric medium on the plasmon resonance of a metal nanostructure. Metal loss limits the sharpness of the plasmon resonance and hence the local-field enhancement [15]. It is also detrimental to many other applications [3,25]. Incorporating a gain medium in a nanostructure to compensate the metal loss is an obvious way to possibly solve the problem. Again, it will be helpful for the design if there are general rules to describe how gain affects a plasmon resonance. We examine the case where the metal nanostructure is completely embedded in a dielectric gain medium since this is the case of maximum achievable gain.

To include the gain in Q, we replace ε_d in Eq. (1) by $\varepsilon_g' + i\varepsilon_g''$ with $\varepsilon_g'' < 0$ and have $\bar{U}_d = \frac{1}{8\pi} \times \int_{\Omega_{\mathrm{dielectric}}} \frac{d(\omega\varepsilon_g')}{d\omega} \overline{E^2} dV$ to account for the dielectric material dispersion. With the help of Eq. (2), we obtain

$$\begin{aligned} Q &= \frac{\int_{\Omega_{\mathrm{metal}}} \frac{d(\omega\varepsilon_m')}{d\omega} \overline{E^2} dV + \int_{\Omega_{\mathrm{dielectric}}} \frac{d(\omega\varepsilon_g')}{d\omega} \overline{E^2} dV}{2(\int_{\Omega_{\mathrm{metal}}} \varepsilon_m'' \overline{E^2} dV - \int_{\Omega_{\mathrm{dielectric}}} |\varepsilon_g''| \overline{E^2} dV)} \\ &= \left(\frac{\varepsilon_m''}{|\varepsilon_m'|} - \frac{|\varepsilon_g''|}{\varepsilon_g'}\right)^{-1} \frac{\omega[\frac{d\varepsilon_m'}{d\omega} + \frac{|\varepsilon_m'|}{\varepsilon_g'} \frac{d\varepsilon_g'}{d\omega}]}{2|\varepsilon_m'|}. \end{aligned} \tag{7}$$

As expected, the gain reduces the loss and enhances Q. But again, the final Q does not depend on the form and shape of the nanostructure as long as the materials and plasmon frequency are fixed. When the gain is large enough that $|\varepsilon_g''|/\varepsilon_g' = \varepsilon_m''/|\varepsilon_m'|$, Q diverges and the nanosystem becomes an oscillator [26]. We then have a simple criterion, $|\varepsilon_g''|/\varepsilon_g' \geq \varepsilon_m''/|\varepsilon_m'|$, for a metal nanostructure in a gain medium to behave like an oscillator or amplifier. This criterion is possible to satisfy in principle, but difficult in practice, considering that metals generally are quite lossy.

It is not clear whether the Q factor can be increased if we look beyond the quasistatic limit and include the wave retardation effect. The larger nanostructure may compromise the localization of the plasmon field. One obvious worry is that the radiation loss tends to increase dramatically with the nanostructure size. For better Q, focus should then be on plasmon resonances that forbid strong electric-dipole radiation. More studies are needed to address these questions.

In summary, we have shown that under the quasistatic approximation, simple general relations regarding plasmon energy distribution, resonance frequency, and linewidth, and effect of optical gain can be derived without the need of specifying the details of a nanostructure. These relations constitute a useful framework that encompasses results from a wide range of studies on specific metal nanostructures. Being nonspecific, they can be used to set limits on the plasmon properties of a given nanostructure, and as a guide in the design to explore plasmon resonances of more complex nanostructures.

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