

## PLASMONIC NEAR-FIELD ENHANCED ABSORPTION AND SCATTERING

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**ABSTRACT.** An important effect when metallic nanoparticles are irradiated by light at the proper frequency is the surface plasmon resonance (SPR), a collective resonant excitation of the nanoparticle's conduction electrons, resulting into enhanced absorption, scattering, and large near-fields close to the nanoparticle surface. We derive analytic closed-form expressions within the framework of a discrete dipole approximation, for two applications involving such nanoparticles: (i) enhancement of semiconductor absorption and (ii) enhancement of Raman scattering, and explore their dependence on nanoparticle shape, distribution and environment. Comparisons with accurate finite-difference time-domain (FDTD) simulations show excellent agreement.

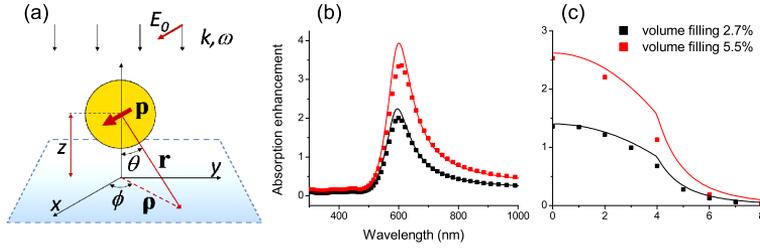
### 1. Introduction

Metallic nanoparticles [1] are of great interest for a variety of technological and biomedical applications. They exhibit strong absorption and field enhancement at their surface plasmon resonance (SPR) frequency, leading to important applications in enhanced spectroscopy [2], enhanced fluorescence [3], chemical and biological sensing [4], catalysis [5]. When placed in arrays, they are capable of guiding light at the extreme sub-wavelength limit, leading to applications in nanophotonic integrated circuits [6]. The main properties of these systems are usually studied within the frame of the Mie theory [7, 8]. For many technological applications it is important to have a simple intuitive formula quantifying the SPR effects, so that optimization of structure is possible. Here we derive such closed-form analytic formulas for two applications: (i) absorption enhancement in organic solar cells, and (ii) surface enhanced Raman scattering in graphene.

### 2. Method

Assume a spherical metal particle of radius  $a$  inside a uniform host material of dielectric constant  $\epsilon_h$ , irradiated by a plane wave of amplitude  $E_0$ , frequency  $\omega$  and polarization along the  $\hat{x}$  direction, as depicted in Fig. 1a. The oscillating incident field will excite an oscillating electric dipole at the nanoparticle center:

$$\vec{p} = \epsilon_0 \epsilon_h \alpha_{np}(\omega) \vec{E} \approx \epsilon_0 \epsilon_h \alpha_{np}(\omega) E_0 \hat{x} \quad (1)$$



**Figure 1.** (a) Schematic of the geometry considered in absorption enhancement. (b) Integrated enhancement on  $z=0$ , for 2 different lattice periodicities:  $L=21.5$  nm ( $f=2.7\%$ ) and  $L=17$  nm ( $f=5.5\%$ ). (c) Integrated enhancement on a plane as a function of  $z$  at  $\lambda = 650$  nm.

where  $E$  is the local field at the nanoparticle, approximately equal to the incident one. The nanoparticle polarizability  $\alpha_{np}$  is described for a sphere within the Mie theory [7, 8] as a function of nanoparticle size and index contrast from the host material. In general, the refractive index of metallic nanoparticles differs from the bulk value due to the reduced free electron relaxation caused by electron surface scattering [9, 10]. To account for this we fit a Drude-Lorentz model to  $\epsilon_{np}(\omega)$  and adjust the corresponding free electron relaxation time according to  $\tau^{-1} \rightarrow \tau^{-1} + v_F/a$ , where  $v_F$  is the metal's Fermi velocity and  $a$  the nanoparticle's radius. Also, since we will assume arrays of nanoparticles at some finite volume filling ratio (say a cubic array of side  $L$ ), the local field a nanoparticle feels is affected by the fields scattered from all the other nanoparticles. This is done most conveniently within the Clausius-Mossotti theory [11] which scales the nanoparticle polarizability according to:

$$\alpha_{np} \rightarrow \alpha_{np}/(1 - N\alpha_{np}/3) \Rightarrow Q \rightarrow Q/(1 - f \cdot Q) \quad (2)$$

where  $N$  is the nanoparticle number density,  $f = 4\pi a^3/3L^3$  is their corresponding volume filling ratio and  $Q$  the normalized polarizability  $Q(\omega) = \alpha_{np}(\omega)/(4\pi a^3)$ .

The dipole fields at position  $\vec{r}$  on a plane at a vertical distance  $z$  are [11]:

$$\vec{E}_d(\vec{r}, \omega) \approx \frac{e^{ikr}}{4\pi\epsilon_0} \left[ \frac{k^2}{r} \hat{\mathbf{r}} \times (\vec{p} \times \hat{\mathbf{r}}) + \left( \frac{1}{r^3} - \frac{ik}{r^2} \right) [3\hat{\mathbf{r}}(\hat{\mathbf{r}} \cdot \vec{p}) - \vec{p}] \right] \quad (3)$$

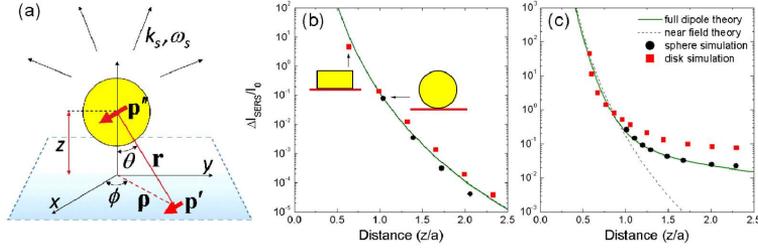
We typically include the near-field term only. We will evaluate two quantities: 1) total absorption enhancement; 2) total Raman enhancement.

### 3. Results

**3.1. Absorption enhancement.** The additional absorption in the plane  $z$  is due to the enhanced near field, and is approximately

$$\Delta A/A_0 \cong \int |\vec{E}_d|^2 dS \quad (4)$$

In the above we ignore cross terms between incident and re-radiated fields. This is justified when strong near-field enhancements are expected. Integrating over the plane surface we



**Figure 2.** (a) Schematic of the Raman emission. (b)-(c) We test the theory against FDTD simulations: suspended spheres (circles) and disks (squares). Black dashed line for near-field term only while solid green line for full dipole field expression. We also consider two particle sizes: in (b) the diameter is 10 nm and in (c) the diameter is 140nm, the disks with aspect ratio 0.57.

get

$$\Delta A(z)/A_0 \cong \frac{1}{4} \sigma |Q|^2 \left( \frac{a^4}{z^4} \right) [5\delta^4 - 2\delta^6] \quad (5)$$

where  $\sigma = \pi a^2/L^2$  is the nanoparticle planar cross section and  $\delta = \min(1, |z|/a)$  makes sure that the integration is always outside the nanoparticle. This result is checked in Fig. 1b against accurate FDTD simulations, as they are described in [12], for 8 nm diameter Au nanoparticles in a host index  $n_h = 2$ , which is appropriate for most organic solar cells. Two square arrangements with sides 21.5 nm and 17 nm are considered, which correspond to volume filling ratios of 2.7% and 5.5% respectively. We assume  $z = 0$  here. Agreement is excellent, except of a slight overestimation from the part of the theory. In Fig. 1c we compare the planar enhancement as a function of  $z$  for a wavelength of 650 nm, slightly detuned from the SPR frequency.

**3.2. Raman enhancement.** We next consider the Raman scattering enhancement on a 2D plane such as single layer graphene (SLG) [12, 13]. Here the relevant enhancing field is the one polarized along the graphene plane, which will excite a dipole field on SLG at the Raman frequency  $\omega_s$ :

$$\vec{p}' = \alpha_R(\omega_s, \omega) \vec{E}_{d\parallel} \quad (6)$$

Upon reradiating at the Raman-shifted frequency  $\omega_s$ , it will get coupled to the nanoparticle and excite a secondary dipole, as shown in Fig. 2a:

$$p'' \propto Q(\omega_s) \alpha_R(\omega_s, \omega) Q(\omega) E_0 a^6 r^{-6} \quad (7)$$

where we only consider the dominant near field term. Upon integrating over the SLG plane, taking into account both emission polarizations and dividing by the signal expecting in the absence of the nanoparticle array, we get the Raman enhancement factor

$$\Delta I_{\text{SERS}}/I_0 \approx \frac{1}{9} \sigma Q^2(\omega) Q^2(\omega_s) \left( \frac{a}{z} \right)^{10} \quad (8)$$

where we only consider the  $z \geq a$  case, i.e. at the closest separation the nanoparticle is resting on the SLG. We compare this result with FDTD simulations of Au nanoparticles suspended in air, shown in Fig. 2b,c for graphene's G peak at  $1580 \text{ cm}^{-1}$ . We consider

two different shapes, spheres and disks, as well as two different sizes, 10 nm and 140 nm. In the absence of an analytical expression for the polarizability of a nanodisk, we use the polarizability of a sphere. The periodicity is set to 23 nm and 320 nm respectively, corresponding to a volume filling ratio of  $f=4.4\%$  for both sphere cases. We note an excellent agreement in the small particle case, but serious discrepancy for the large particle case. In order to remedy that, we performed the SERS calculation including all orders of the dipole fields, and the result is plotted in Fig. 2c with a green line. We recover an excellent agreement in the case of spheres, and as expected, less agreement for the case of disks.

#### 4. conclusions

We derived analytical closed form expressions for the integrated field enhancement around metallic nanoparticles for two applications: (i) absorption enhancement in organic solar cells and (b) surface enhanced Raman scattering in graphene. Detailed comparisons with accurate FDTD simulations confirm the approximations used and prove the usefulness of the derived expressions in optimizing plasmonic phenomena.

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