Analysis of Optical Properties of 2D Ordered Plasmonic Nanoparticle Systems Using a 3D Pseudospectral Time-Domain Scheme

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1. Introduction

Optical properties of metal nanoparticle clusters have long attracted much research interest. One important topic is the surface-enhanced Raman scattering (SERS) first observed in 1974 [1]. The phenomenon comes from the interaction between the rough metal surface and its nearby molecules, from which unknown molecules or micro-organisms can be detected using such SERS tool. In 1997, extremely high SERS signals were observed at some so-called “hot junctions” in the single-molecule SERS experiment [2]. It reported that the enhancement factor used to estimate amplification could reach ~10^{14} times so that it could be promoted as a potential tool to monitor the dynamic changes of the molecule structure. However, neither the colloidal system studied in that experiment [2] nor roughened metal surfaces can exhibit efficient Raman enhancement for sensing molecules. Thus, how to create a reliable, stable, and uniform SERS signal became the succeeding issue. Recently, fabrication of two-dimensional (2D), high density, plasmonic nanoparticle arrays on a substrate that can provide such signals have been reported [3]. Such SERS-active substrates bring us a new opportunity to comprehend the detailed mechanism of SERS further. In this research, we study how to characterize optical properties of these substrates by numerical simulation.

Due to the limit of fabrication, the nanoparticle systems reported in [3] did not order completely and the shapes of nanoparticles were not uniform either, which became more obvious when the gap between nanoparticles got smaller. The shapes of nanoparticles and the inter-particle spacings should be described by some statistical distributions. Such distributions would make resonance wavelengths red-shift and the peak of the resonance response much broader than what has been pointed out in the literature [4]. Before establishing an effective procedure to simulate such complicated environment, two sources of unnecessary inaccuracy should be better avoided. The first is the material dispersion model. Although most literatures used the Drude model to approach the dielectric constants of noble metals at optical frequencies, the deviation induced by the bound electrons is often obvious. In our study, the additional Lorentz terms are included in the material model to reduce such deviation. The second comes from the numerical treatment of metallic-dielectric interfaces. With the aid of the domain decomposition technique, a high-accuracy numerical scheme, the Legendre pseudospectral time-domain (PSTD) method proposed in [5,6] is employed to properly treat the interfaces. Moreover, since denser mesh grids appear near the interface, the method is particularly appropriate to deal with the metallic-dielectric interfaces.

At present, 3D electromagnetic (EM) simulations are still quite computer-time consuming. Thus, besides the PSTD simulation, a dipole model is also introduced to do rapid theoretical estimations of optical properties of nanoparticle systems. The dipole-model theoretical prediction not only cross-checks the PSTD simulation, but also examines whether the dipole approximation is enough to capture the coupling effect between nanoparticles. We will discuss optical scattering spectra for different interparticle spacings.

2. Material Model and Polarizability of Systems

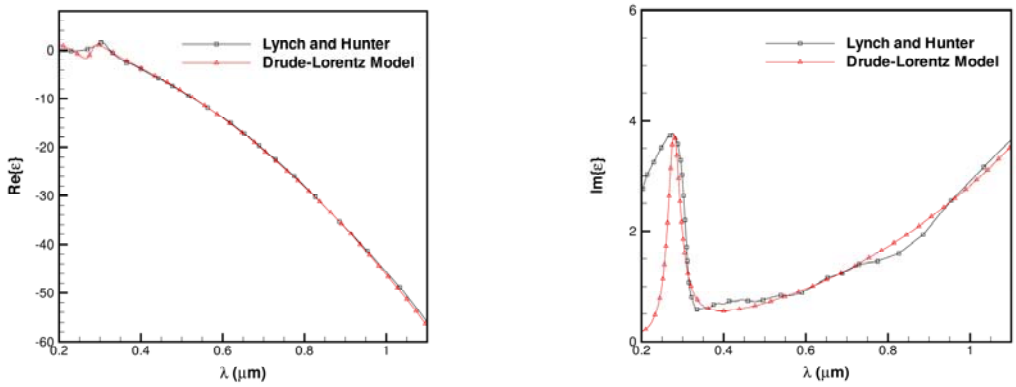
The relative permittivity formula of the Drude-Lorentz (D-L) model is expressed as

$$\varepsilon_{DL}(\omega) = \varepsilon_{\infty} - \frac{\omega_p^2}{\omega(\omega + i/\tau)} + \sum_{j=1}^{k} \frac{f_j \omega_p^2}{(\omega_j^2 - \omega^2) - i\omega\Gamma_j} \tag{1}$$

where ε_{∞} is the high-frequency limit of the dielectric constant, ω_p is the plasma frequency, τ is the life time, and k is the number of oscillators with oscillator j characterized by frequency ω_j, strength f_j, and the damping constant Γ_j. To obtain the values of these parameters, we combine two optimization schemes to carry out the curve-fitting action on the measured data of silver provided in [7]. Firstly, we define an objective function

$$\Psi = \sum_{\omega_j} \left\{ \left(\mathrm{Re}\left[\varepsilon_{\exp}(\omega_j) - \varepsilon_{DL}(\omega_j) \right] \right)^2 + \left(\mathrm{Im}\left[\varepsilon_{\exp}(\omega_j) - \varepsilon_{DL}(\omega_j) \right] \right)^2 \right\} \tag{2}$$

where $\varepsilon_{\exp}$ and ε_{DL} represent measured data and the D-L model values, respectively. The ω_j's are the set of discrete frequency values for getting the relative permittivities. The parameters to be determined are then refined by employing the genetic algorithm and the nonlinear least squares method alternately until good results are obtained. However, for relieving the computational loading and not effecting the results, we manually modify the parameters and get rid of the redundant Lorentz terms at the same time. The parameters obtained are: $\varepsilon_{\infty} = 3.07$, $\omega_p = 83996.63335 \times 10^{12}$ rad/sec, $\tau = 0.01485 \times 10^{-12}$ sec, $f_1 = 0.065$, $\omega_1 = 7793.80694 \times 10^{12}$ rad/sec, $\Gamma_1 = 37116.08 \times$, 10^{12} rad/sec, $\omega_2 = 42502.97395 \times 10^{12}$ rad/sec, $f_2 = 0.124$ and $\Gamma_2 = 5730.73812 \times 10^{12}$ rad/sec. Figure 1 shows the comparison between the measured relative permittivity values (black lines) and the obtained D-L model values (red lines) in the wavelength region from 0.2 μm to 1.1 μm. Good agreement is seen for wavelengths larger than 0.3 μm.



(a) (b)

Figure 1: The permittivity of silver in the optical wavelength region.
(a) The real part. (b) The imaginary part.

The scenario of our simulation is depicted in Fig. 2 (a) which shows a 2D nanoparticle square-lattice array extended to infinity in the *x-y* plane with an incident polarized electromagnetic wave propagating along the direction of the minus *z*-axis. We consider the structure of a square unit cell with periodic boundary conditions (PBCs) parallel to the *z*-axis, as shown in Fig. 2 (b). The particle is taken as a sphere with the fixed diameter, D = 25 nm and various sizes of gap, W = 25, 20, 15, 10, and 5 nm are considered. The lattice constant is $a = D + W$. The relative permittivities for air and the silver are $\varepsilon_1 = 1$ and $\varepsilon_2 = \varepsilon_{DL}(\omega)$, respectively.

The estimation of the effective polarizabilities of the 2D systems by the dipole model [4] is described as follows. The dipole moment $\vec{p}_i$ induced in particle i at $\vec{r}_i$ is given by $\vec{p}_i = \vec{\alpha}_i(\omega)\vec{E}_{loc}(\vec{r}_i)$, where $\vec{E}_{loc}(\vec{r}_i)$ is the local field at particle i and $\vec{\alpha}_i(\omega)$ is its polarizability.

The contribution to the local electric field includes two parts, one is the incident field and the other is the field from the rest of particles. So the local field can be expressed as

$$\vec{E}_{loc}(\vec{r}_i) = \vec{E}_{inc}(\vec{r}_i) + \vec{E}_{other,i} = \vec{E}_{inc}(\vec{r}_i) - \sum_{j(\neq i)} \overleftrightarrow{U}\left(\vec{r}_i - \vec{r}_j\right) \bullet \vec{p}_j \tag{3}$$

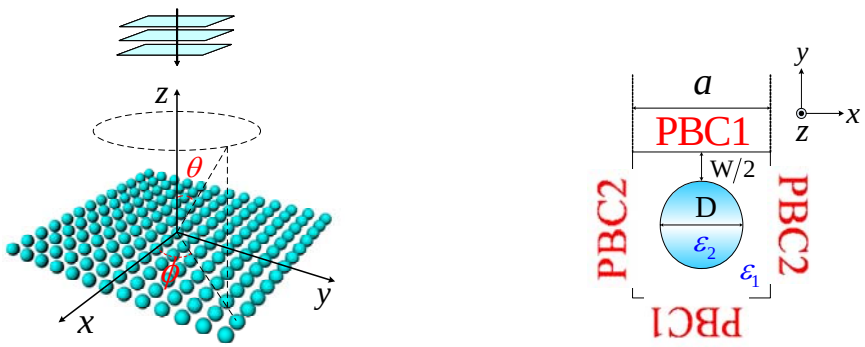
where $\overleftrightarrow{U}\left(\vec{r}_i - \vec{r}_j\right)$ is a tensor for describing the dipole-dipole interaction. Inserting (3) into $\vec{p}_i = \overleftrightarrow{\alpha}_i(\omega)\vec{E}_{loc}(\vec{r}_i)$ and assuming $\vec{p}_i = \vec{p}_j$ due to the fact that all particles are identical, we obtain

$$\vec{p}_i = \frac{\overleftrightarrow{\alpha}_i(\omega)}{1 + \overleftrightarrow{\alpha}_i(\omega)\sum_{j(\neq i)} \overleftrightarrow{U}\left(\vec{r}_i - \vec{r}_j\right)} \vec{E}_{loc}(\vec{r}_i) \equiv \overleftrightarrow{\alpha}_{eff}\vec{E}_{inc}(\vec{r}_i). \tag{4}$$

Since the condition $ka << 1$ is held, where k is the free-space wavenumber, and the wave is normally incident, only the transverse-mode polarizability denoted as $\alpha_{eff}^{\parallel}(\omega)$ is considered. The expression of the polarizability can be found to be [4]

$$\alpha_{eff}^{\parallel}(\omega) = \frac{\alpha_i(\omega)}{1 - \frac{1}{2}\alpha_i(\omega)U_0} \tag{5}$$

where $U_0 = 9.03a^{-3}$. The effective polarizability will be utilized to estimate the reflectance.

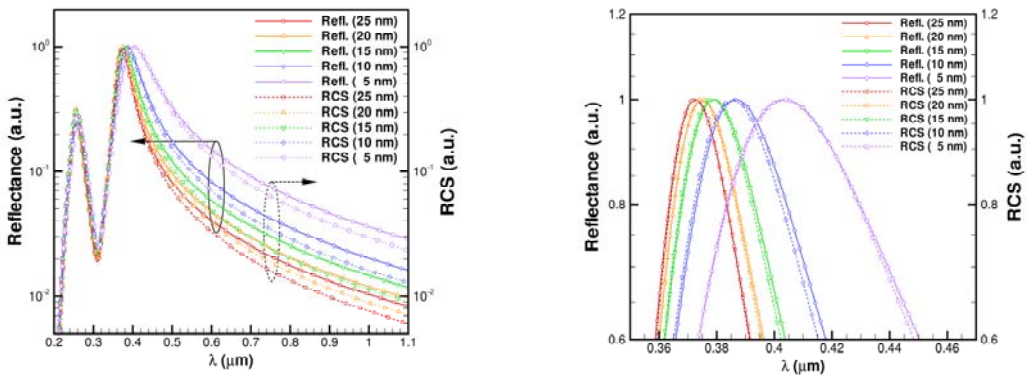


(a) (b)

Figure 2: (a) Scenario of an electromagnetic wave incident onto a 2D system of nanoparticles. (b) The top view of the unit cell with a nanoparticle.

3. Numerical Results

Many experimental measurements involve far fields. In our numerical simulation, we also focus on the behaviour of backscattered far fields. The monostatic radar cross section (RCS) is calculated using the PSTD method and compared with the reflectance estimated by the dipole model. Utilizing the effective polarizability described in Section 2, the reflectance $|r|^2$ relative to the polarizability can be expressed as $|r|^2 = \left|A\alpha_{eff}^{\parallel}(\omega)\right|^2 \Big/ \left|1 - A\alpha_{eff}^{\parallel}(\omega)\right|^2$, where $A = 2\pi\omega i / ca^2$ [4]. According to the definition of the RCS, the above reflectance is proportional to the monostatic RCS at the angle opposite to the incident one in these 2D periodic structures. Figure 3 shows the comparison between the normalized reflectance and the normalized monostatic RCS for various gap sizes. The results reveal that the dipole approximation models such structures well. In other words, the higher mulitpoles have minor contributions to the coupling effect between the nanoparticles. As to the effect of gap size, it is seen that the resonant frequency peaks show red-shift and the spectral width becomes larger as the gap gets smaller. Here also notice that these peaks fall in the wavelength region around 0.4 μm, and the employment of correct material model for this region is essential. If only the Drude model is adopted, the deviation in the calculated peak wavelength is found to be about 20 nm.



(a) (b)

Figure 3: (a) The comparison between the normalized reflectance from the dipole model and the normalized monostatic RCS from PSTD simulations. (b) Enlargement of (a) for viewing the peaks.

4. Conclusion

We have applied the 3D Legendre pseudospectral time-domain scheme to study the optical properties of 2D plasmonic nanoparticle square arrays with different gap sizes. Numerical simulation results have been compared with a theoretical dipole model which provides quick analysis, and good agreement was obtained. The high-accuracy numerical scheme is especially suited for dealing with metal-dielectric interfaces in plasmonics problems. The more precise Drude-Lorentz model has been introduced to provide a better material model and thus more accurate calculation in the wavelength region from visible to the near infrared.

Acknowledgments

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