Fluorescence characteristics of a molecule in the vicinity of a plasmonic nanomatryoska: nonlocal optical effects

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Abstract

The fluorescence characteristics of a dipole molecule in the vicinity of a spherical multilayered metallic nanoshell (a plasmonic nanomatryoska) of ultra-small dimensions is studied via electrodynamic modeling, where we have computed the fluorescence decay rates, the shifts in emission frequency, and the overall fluorescence yields for molecular dipoles of both tangential and radial orientations. Our focus is on structures of ultra small dimensions in order to elucidate the possibly novel nonlocal optical effects in such a phenomenon. The results show that at very close distances between the molecule and the nanoshell, the nonlocal effects in general lead to smaller structure-induced effects with broadened and blue-shifted plasmonic resonances. These effects include overall smaller induced decay rates, smaller red-shifts in emission frequency, and somewhat larger fluorescence yields at low emission frequencies. Physical interpretation of our simulation results is provided.

Key Words: Molecular fluorescence; Metallic nanoshells; Optical properties; Nonlocal response

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Introduction

Since the metallic nanoshell was first fabricated in 1998 [1], various shell structures of higher complexity have been introduced in the last decade with the promise of leading to greater flexibility in their tunable plasmonic resonances, as well as in the enhanced optical fields they produce. These include, for example, the multishell structure (the "nanomatryoska") [2] and the spheroidal nanoshell structure (the "nanorice") [3] which have received appreciable attention among researchers in nanoplasmonics in recent years.

While the optical properties of these novel plasmonic structures are intriguing, to our knowledge, except for a few previous works [4 - 9], these have been studied most of the time via far-field excitation in the literature in which the absorption, scattering and extinction properties of these structures are calculated or measured [10]. It is well-known that due to the small dimensions of these structures compared to the optical wavelengths, the dipole response of them is usually sufficient to account for observations in far-field experiments which makes the analysis relatively simple. However, there are certain optical phenomena such as molecular fluorescence in the vicinity of these nanoshells which will involve near-field interactions with the structures [4-9], and which can find significant applications in processes like molecular sensing and labeling.

It is the purpose of the present work to present a systematic theoretical study of the fluorescence characteristics of a dipole molecule in the vicinity of a nanomatryoska of ultra small dimensions, generalizing several recent works which were limited to either a solid metallic nanoparticle [6] or a single-layered nanoshell [7]. Our main goal is to elucidate the possibly novel nonlocal optical effects on this process which have not been studied in details previously in the literature for such a multilayer plasmonic system. The significance of such nonlocal

effects, however, has also been the focus in the above-cited recent works [6, 7] where simpler plasmonic nanostructures had been considered. Although nonlocal effects were incorporated in the general formulation of the dipole-multishell problem in previous works [4, 5]; such effects on the fluorescence characteristics were only qualitatively discussed in [4], and the dipole is considered to be embedded in these shell structures while numerical studies were limited to a single silver shell embodying the fluorescing dipole in [5]. Here we consider the molecule to be outside in close proximity to such a structure and we focus particularly on the interference effects from more than one metallic shell. Our interest is in the possibility of using these nanoparticles as an external agent for the modification of molecular spectroscopic properties. We shall see that since many higher order multipole interactions will be involved between the molecule and the nanostructure, these nonlocal effects will be more significant compared with those in the case of far-field phenomenon [7]. Referring to this latter phenomenon, there exists a long history of literature including the recent works on the optical properties of various metallic nanoparticle systems [11]. Here we focus, however, on the effects on near fields and our approach is based on a theory we recently formulated [12] for this multishell system, which we shall briefly review in the following section in order to make the presentation self-contained.

Theoretical Modeling

We refer our problem to Fig. 1, where a fluorescing molecule is modeled as an emitting dipole which is located in close proximity to a nanomatryoshka. Since all the characteristic dimensions (the nanoshell size, the molecule-nanoshell distance, …etc.) are small compared to the emission wavelengths, we shall describe the interacting system within a long wavelength approximation. Our interest is in the calculation of various fluorescence characteristics of the

molecule which include: the decay rates (γ), the emission frequency shifts ($\Delta\omega$), and the fluorescence yield (γ^{FL}) --- all normalized to the rates for a free molecule.

Following the previous phenomenological models established in the literature [13], the above quantities can be obtained in the following form depending on the orientation of the molecular dipole with respect to the spherical structure [14]:

$$\frac{\gamma}{\gamma_0} = 1 + \frac{3q}{2k^3}\,\mathrm{Im}(\mathcal{G}), \tag{1}$$

$$\frac{\Delta\omega}{\gamma_0} = -\frac{3q}{4k^3}\,\mathrm{Re}(\mathcal{G}), \tag{2}$$

$$\frac{\gamma^{FL}}{\gamma_0^{FL}} = \left|\frac{E}{E_0}\right|\left(\frac{\gamma_R}{\gamma}\right), \tag{3}$$

where q is the intrinsic quantum yield of the molecule, k the emission wave number, and the $\mathcal{G}$ factor is dependent on the molecular orientation and is defined as follows:

$$\mathcal{G} = \sum_{\ell} f_\ell \frac{\alpha_\ell}{r^{2\ell+4}}, \tag{4}$$

where α_ℓ is the ℓ *th* pole polarizability of the nanomatryoshka, r is the radial coordinate of the molecular dipole, and the factor f_ℓ is defined as follows:

$$f_\ell = \begin{cases} (\ell+1)^2, & \text{for radial dipole} \\ \ell(\ell+1)/2, & \text{for tangential dipole} \end{cases}. \tag{5}$$

The other quantities in (3) which include the field enhancement ratio and the radiative decay rate of the molecule are given by the following expressions:

$$\left|\frac{E}{E_0}\right| = \left(\frac{\gamma_R}{\gamma_0}\right) = \begin{cases} \left|1+\dfrac{2\alpha_1}{r^3}\right|^2, & \text{for radial dipole} \\ \left|1-\dfrac{\alpha_1}{r^3}\right|^2, & \text{for tangential dipole} \end{cases} . \qquad (6)$$

Note that these quantities in (6) depend only on the dipole polarizability of the nanomatryoshka in the long wavelength approximation according to the models of Gersten and Nitzan [13].

Hence in order to study the modified fluorescence characteristics due to interaction between the molecule and the nanostructure, one has to calculate the multipole polarizability of the nanomatryoshka. In a recent work [12], we have formulated exactly such a nonlocal theory for the calculation of this quantity which we shall briefly summarize in the following.

For a system of multi-shell of n layers, with each layer being described by a *nonlocal* (isotropic) dielectric function $\varepsilon_j(k,\omega)$, $j = 1, 2, \ldots, n+1$, the overall nonlocal polarizability can be obtained with the application of two previously-published results in the literature: the result for the nonlocal polarizability of a single-layered spherical shell [15], in combination with certain effective medium theory [16]. The result thus obtained can be expressed in the following form [12]:

$$\alpha_\ell = r_{n+1}^{2\ell+1} \frac{b_{n+1}(1-\varepsilon_h / a_{n+1})[\ell\xi_n + (\ell+1)c_{n+1}]r_{n+1}^{2\ell+1} + c_n[(\ell+1)(\xi_n - b_{n+1}) + \ell\varepsilon_h(\xi_n / b_{n+1} - 1)]r_n^{2\ell+1}}{b_{n+1}[1+(\ell+1)\varepsilon_h / \ell a_{n+1}][\ell\xi_n + (\ell+1)c_{n+1}]r_{n+1}^{2\ell+1} + c_{n+1}(\ell+1)[\varepsilon_h - b_{n+1} + \xi_n(1-\varepsilon_h / b_{n+1})]r_n^{2\ell+1}} \qquad (7)$$

where ε_h is the local dielectric function of the host (background) medium, ξ_n is an effective local dielectric response defined as follows:

$$\xi_n = \frac{\pi}{2(2\ell+1)} \frac{1}{r_n} \left[\int_0^\infty \frac{j_\ell(kr_n) j_\ell(kr_n)}{\varepsilon_n^s(k,\omega)} dk \right]^{-1}, \tag{8}$$

where j_ℓ is the spherical Bessel function, and $\varepsilon_n^s(k,\omega)$ is a certain effective nonlocal function which represents the averaged nonlocal dielectric response of the materials inside the region $0 < r < r_n$. For $n=1$ we have $\varepsilon_1^s(k,\omega) = \varepsilon_1(k,\omega)$.

By applying an effective medium approach [16], we have shown that ξ_n can be obtained iteratively according to the following scheme [12]:

$$\xi_n = \frac{d_n - (1+1/\ell) a_n q_n}{1+q_n} \tag{9}$$

where

$$q_n = \frac{e_n \ell (1-F_n) - \varepsilon_h [\ell + (\ell+1) F_n]}{d_n (\ell+1)(1-F_n) + \varepsilon_h [\ell + (\ell+1) F_n]} \frac{d_n^2}{a_n e_n} \left(\frac{r_{n+1}}{r_n} \right)^{2\ell+1} \tag{10}$$

and

$$F_n = \frac{f_n (1-\varepsilon_h / e_n)[\ell \xi_{n-1} + (\ell+1) c_n] r_{n+1}^{2\ell+1} + c_n [(\ell+1)(\xi_{n-1} - f_n) + \ell \varepsilon_h (\xi_{n-1} / f_n - 1)] r_{n-1}^{2\ell+1}}{f_n [1 + (\ell+1)\varepsilon_h / \ell e_n][\ell \xi_{n-1} + (\ell+1) c_n] r_{n+1}^{2\ell+1} + c_n (\ell+1)[\varepsilon_h - f_n + \xi_{n-1}(1-\varepsilon_h / f_n)] r_{n-1}^{2\ell+1}}. \tag{11}$$

The parameters a_n, b_n, c_n, d_n, e_n, f_n are defined as: $a_n = E_{\ell,n}^{n,n}$, $b_n = E_{\ell,n}^{n-1,n}$, $c_n = E_{\ell,n}^{n-1,n-1}$, $d_n = E_{\ell,n}^{n,n+1}$, $e_n = E_{\ell,n}^{n+1,n+1}$, $f_n = E_{\ell,n}^{n-1,n+1}$, where $E_{\ell,n}^{p,q}$ is derived from the effective local response for a single-layered shell [15]:

$$E_{\ell,n}^{p,q} = \frac{\pi}{2(2\ell+1)} \frac{r_p^{\ell}}{r_q^{\ell+1}} \left[\int_0^{\infty} \frac{j_\ell(kr_p) j_\ell(kr_q)}{\varepsilon_n(k,\omega)} dk \right]^{-1} \tag{12}$$

Hence by starting with $\xi_1 = a_1$ and going through the above iterative scheme, one can ultimately calculate ξ_n and obtain the ℓ *th* pole polarizability from Eq. (7), and hence the modified fluorescence characteristics from Eqs. (1) – (6).

Numerical results and discussion

To illustrate how an emitting molecule can interact with a nanomatryoshka, we have considered a four-layered nanostructure composed of glass-silver-glass-silver with 1 nm thickness for each layer as well as the core radius. To account for the nonlocal dielectric response for silver, we adopt the following hydrodynamic model:

$$\varepsilon(k,\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i\Gamma) - v_0^2 k^2}, \tag{13}$$

which reduces to the local Drude model when the "nonlocality parameter" $v_0 = 0$. The definition of this and other quantities (and their respective values for silver) are well-known and were given in [12]. The corresponding real and imaginary part of (13) can be obtained as:

$$\varepsilon_R \equiv \mathrm{Re}\,\varepsilon(k,\omega) = 1 - \frac{\omega_p^2 \alpha^2}{\alpha^4 + \omega^2\Gamma^2}, \qquad \varepsilon_I \equiv \mathrm{Im}\,\varepsilon(k,\omega) = \frac{\omega_p^2 \omega\Gamma}{\alpha^4 + \omega^2\Gamma^2}, \tag{14}$$

where $\alpha^2 \equiv \omega^2 - v_0^2 k^2$. It is possible to redefine a more accurate semi-empirical nonlocal function to replace (13) by resorting to experimental data [11], but for simplicity, here we just use (13) as a model calculation. Furthermore, we shall assume the molecule to be placed at close proximity at a distance of 1 nm from the surface of the nanomatryoshka, and consider both the radial and tangential orientations of the molecule.

Figure 2 shows the results for the normalized decay rate as a function of emission frequency, for both the cases of (a) radial and (b) tangential molecular dipole. Note that while the tangential dipole always experiences a greater decay rate at close distances due to opposite relative orientations between the source and image dipoles, the typical nonlocal effects always lead to blue-shifted and broadened resonances, as well as appreciable smaller structure-induced effects. The physical origin accounting for the observed spectral behavior is mainly from the deeper penetration (into the particle) of the induced charges in the case of nonlocal response, which leads to an effective decrease in the permittivity as well as an increase in damping for the free electrons [11]. This can also be seen mathematically from Eq. (14) in which the dipolar surface plasmon resonance condition $\varepsilon_R = -2$ yields a resonance frequency $\omega_{SP} > \omega/\sqrt{3}$ for $v_0 \neq 0$; as well as a larger ε_I resulting in larger damping (hence broadened resonances) and weaker surface-induced field. Note also that the *two*-peak resonance behavior (in both the local and nonlocal cases) arises from a complicated mixing of contributions from many different multipole responses of the nanomatryoshka. It is of interest to compare the present results with those obtained previously for the case of a single-layered nanoshell [7], where only *one* peak appears. We expect as the number of metallic shells increases in the nanomatryoshka structure,

more of these resonance peaks will appear confirming the greater tunability for these more complex structures.

Figure 3 shows similar plots but for the emission frequency shifts of the molecule. First it is noted that the nanomatryoshka-induced shifts are all red-shifts at low emission frequencies, a well-known result arising from the fact that the interaction between a static dipole with its image from a metallic surface always tends to lower the energy of the source dipole. Also this interaction is weaker in the case for tangential dipole, leading to smaller red shifts in this case. Small blue shift can take place at higher frequencies due to retardation effects, which result in some lagging between the alignment of the source and image dipoles (or anti-alignment in case of tangential dipoles). Note that similar *two*-peak resonance behavior also appears here as in Fig. 2. Again, just like the case for the decay rates, the nonlocal effects will in general lead to smaller structure-induced effects with broadened and blue-shifted resonances, with the same physical origin for these effects as explained in the above.

Finally, we study the fluorescence yield of the molecule in the vicinity of the nanomatryoshka. It is clear that at such a close distance to the metallic nanoshell, the nonradiative damping is so severe, that the quantum yield (i.e. the factor $\left(\gamma_R / \gamma\right)$ in Eq. (3)) becomes so small [14], leading to a strong suppression of fluorescence yield as shown in Fig. 4. Moreover, the resonance structure of this spectrum is predominated by the dipole resonance of the nanomatryoshka as illustrated by the four peaks in the figure (particularly clear in Fig. 4(a) for the radial dipole case). This can be understood from examining the results in Eqs. (3) and (6) above which reveal the strong dependence of this fluorescence yield on the dipole polarizability of the nanoshell (α_1) through both the field-enhancement factor and the radiative rate. Again,

the nonlocal effects in this case simply shift these coupled (hybridized) dipole resonances slightly towards the blue, but not necessary leading to lower fluorescence yields since nonlocal effects can lead to a relatively greater quantum yield (the ratio of the decay rates on the RHS of Eq. (3)). This is due to the decrease in the total decay rate (see Fig. 2) arising from the weakened surface induced fields, which is in turn caused by the deeper penetration of the nonlocal induction of charges as explained in the above. Furthermore, since the radiative rates for tangential dipoles are in general less than those for the radial ones, the fluorescence yields for the radial dipoles are overall stronger. All these are particularly clear for low emission frequencies when retardation effects are insignificant in the long-wavelength limit as revealed from the results in Fig. 4.

Conclusions

In this work, we have applied the model we recently formulated [12] to study the nonlocal optical effects on the behavior of a fluorescing molecule in the vicinity of a multilayered metallic nanoshell (nanomatryoshka) of ultra small sizes. The main limitations of our model are the same as those from the "Specular Reflection Model [15]" as discussed in the recent study [11]. These include the assumptions of translational invariance and isotropy in the nonlocal response of the metal, so that one can make use of the bulk dielectric function $\varepsilon(k,\omega)$ to account for the nonlocal effects. In addition, this approach [15] has adopted the so-called "Semiclassical Infinite Barrier (SCIB)' approximation which leads to an unwanted feature with a discontinuity in the charge distributions at the interfacial boundaries. Alternative and improved "nonlocal formalisms" exist as discussed in [11] (e.g. the *d*-function formalism of Feibelman [19]).

Aside from the familiar blue-shifts in the plasmon resonances due to these effects, one significant conclusion from our model study is that in spite of the serious damping of the radiative rates for molecules located in such close proximity to a metallic nanostructure, the nonlocal effects will help to temper somewhat the total induced decay leading to slightly greater fluorescence yields [6]. In light of the results from our present modeling, we believe that future fluorescence experiments similar to those performed for a single metal particle [17, 18] will be of interest, with the particle being replaced by a nanomatryoshka, so that the numerical results discussed in our present work can be tested.

Acknowledgments

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Figure captions

[1] The geometry of the fluorescence system.

[2] Normalized decay rate for an emitting dipole located at 1 nm above a four-layer shell with (a) radial and (b) tangential orientation, respectively. The shell is made of (from core) glass/silver/glass/silver with radii $r_1 = 1$ nm, $r_2 = 2$ nm, $r_3 = 3$ nm and $r_4 = 4$ nm.

[3] Normalized frequency-shifts in the emission frequency of the molecule for the same configuration as in Fig. 2 with (a) radial and (b) tangential orientation, respectively.

[4] Normalized fluorescence yield of the same configuration as in Fig. 2 with (a) radial and (b) tangential orientation, respectively.

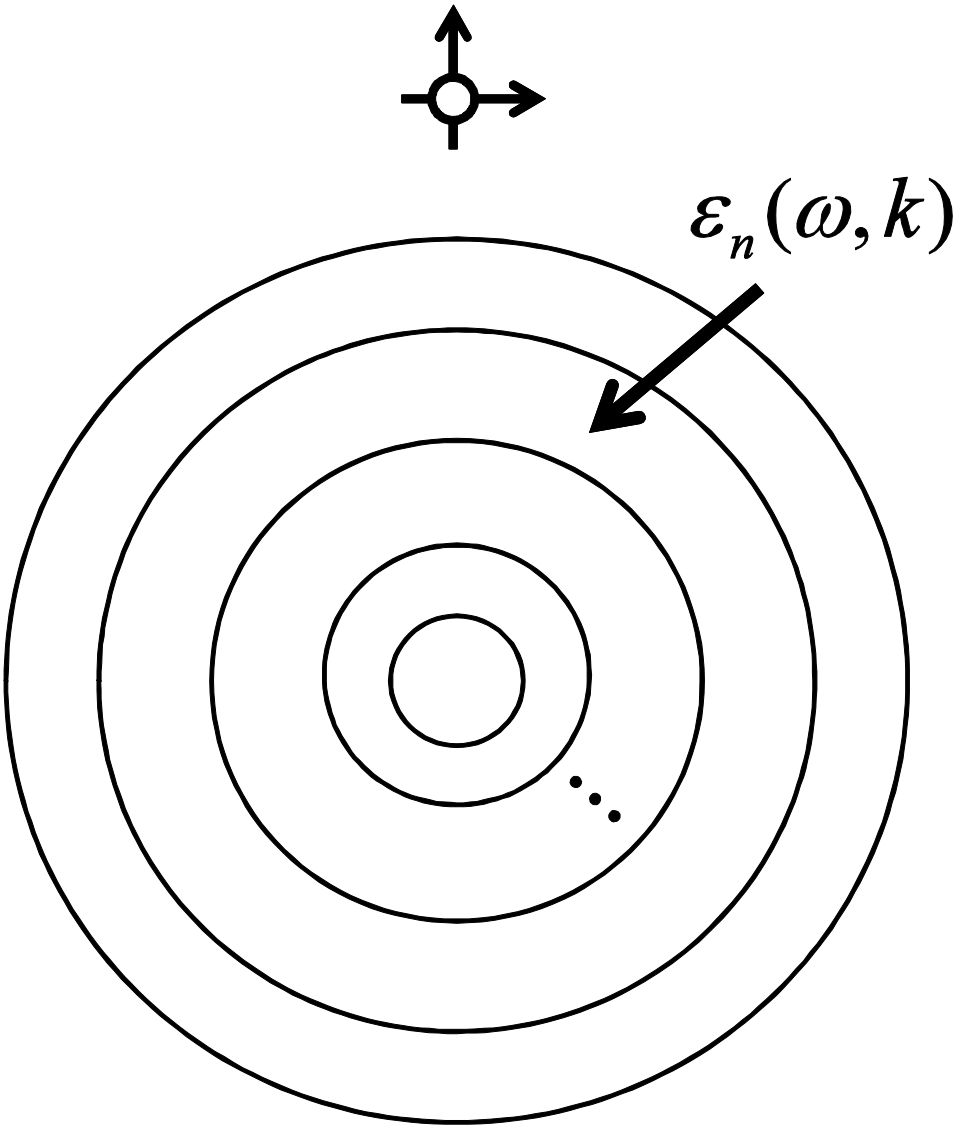
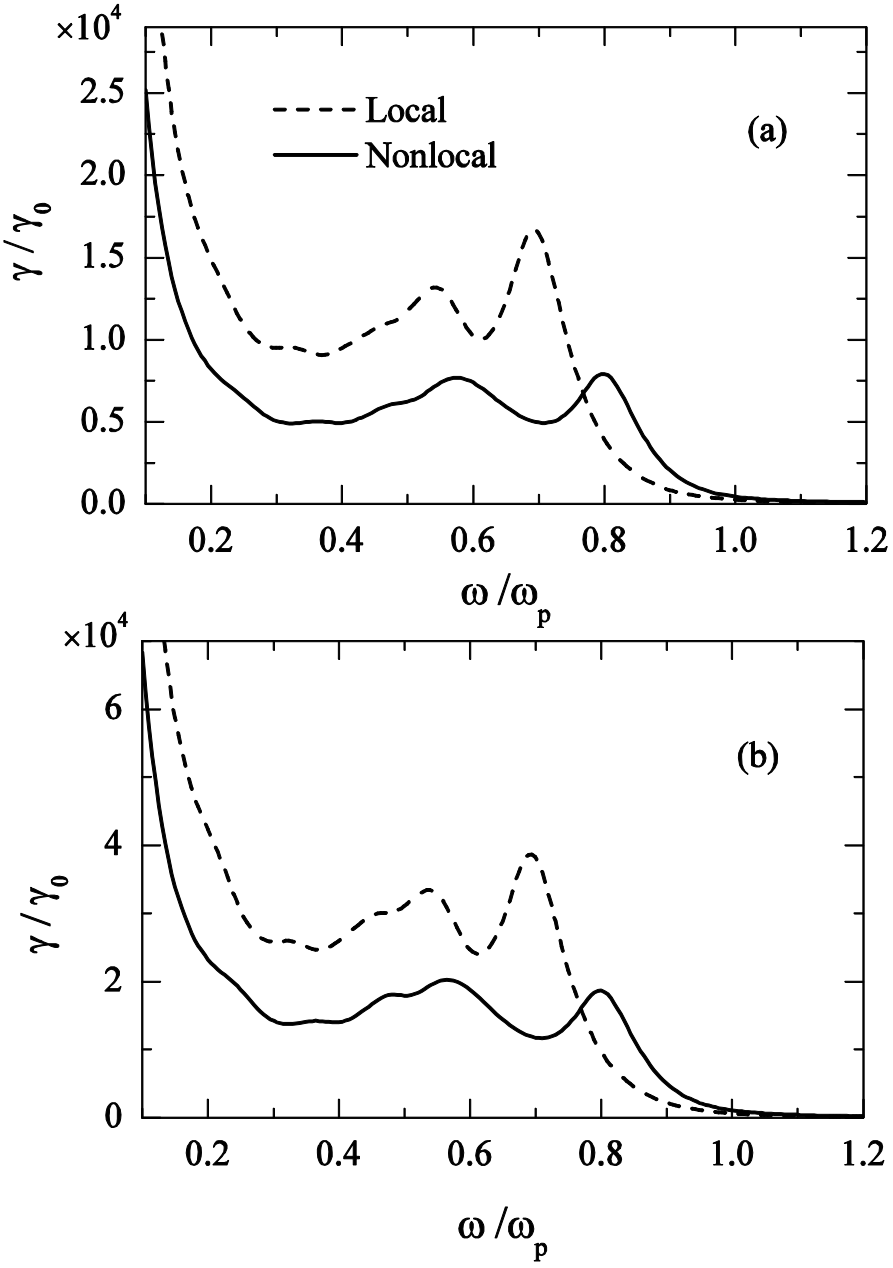


Fig. 1


×10^4
2.5
2.0
1.5
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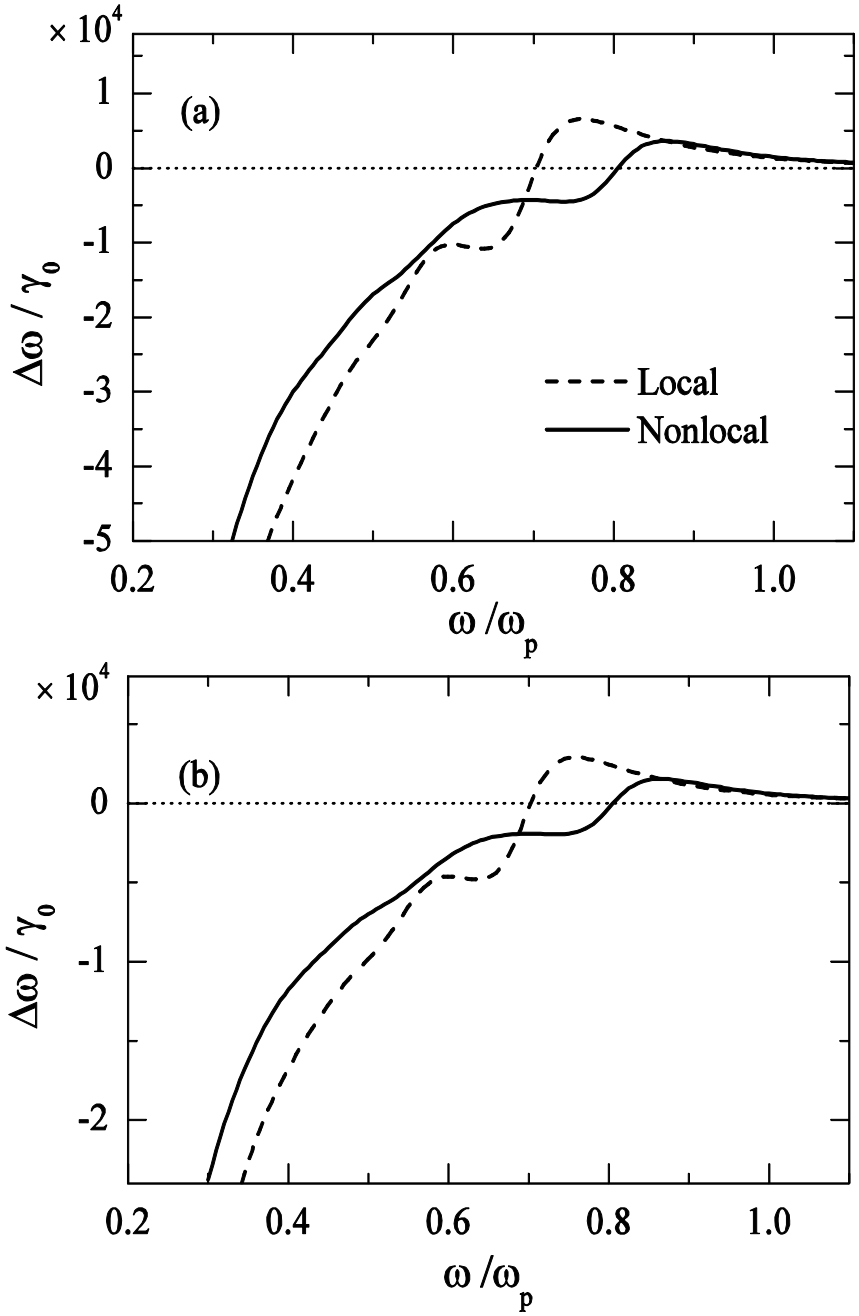
γ / γ_o
Local
Nonlocal
(a)
0.2
0.4
0.6
0.8
1.0
1.2
ω /ω_p
×10^4
6
4
2
0
γ / γ_o
(b)
0.2
0.4
0.6
0.8
1.0
1.2
ω /ω_p

Fig. 2


× 10^4
1
0
-1
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-3
-4
-5
(a)
Δω / γ_o
Local
Nonlocal
0.2
0.4
0.6
0.8
1.0
ω /ω_p
× 10^4
0
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(b)
Δω / γ_o
0.2
0.4
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0.8
1.0
ω /ω_p

Fig. 3

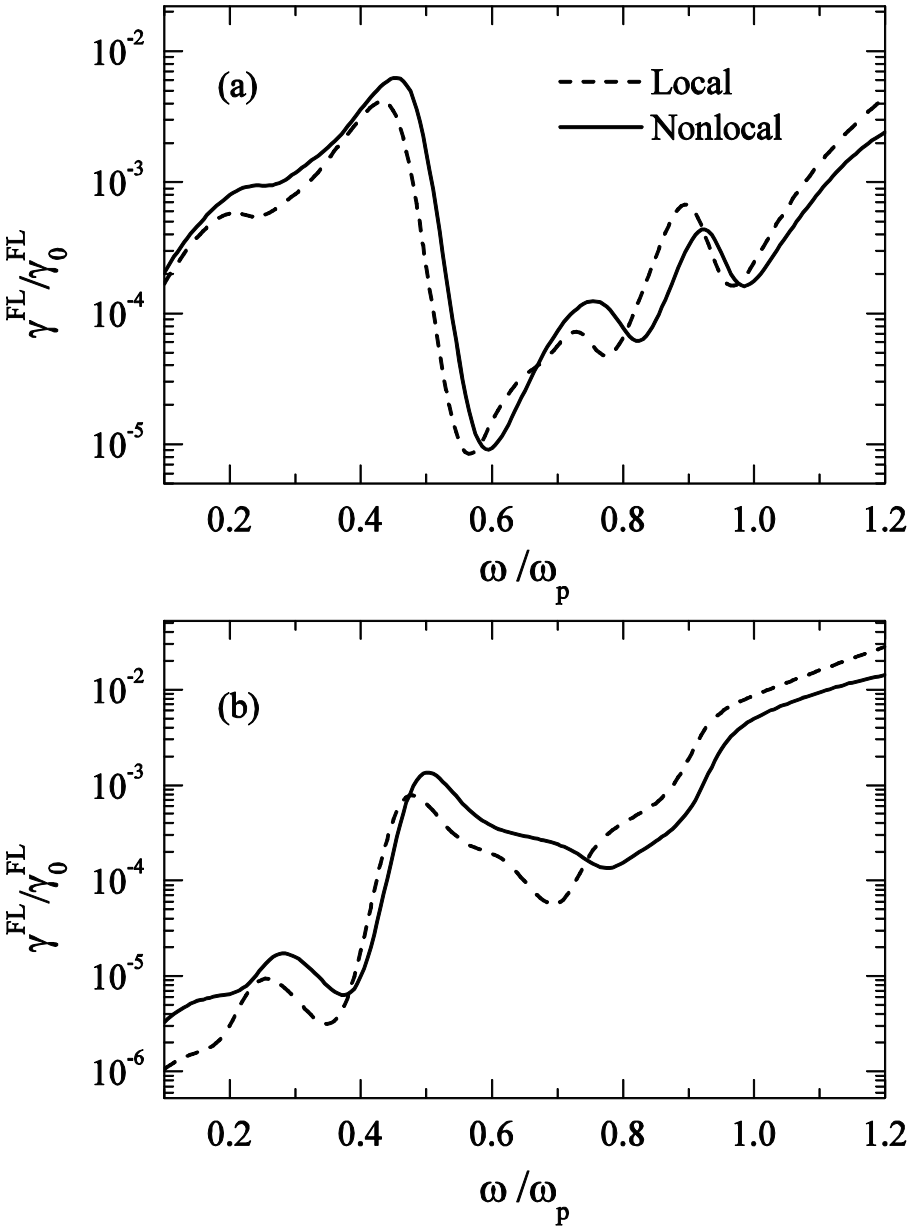
(a)
Local
Nonlocal
10^{-2}
10^{-3}
10^{-4}
10^{-5}
$\gamma^{FL}/\gamma_0^{FL}$
0.2
0.4
0.6
0.8
1.0
1.2
ω/ω_p
(b)
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
$\gamma^{FL}/\gamma_0^{FL}$
0.2
0.4
0.6
0.8
1.0
1.2
ω/ω_p

Fig. 4