Plasmonic nanostructures: local versus nonlocal response

Giuseppe Toscano[a], Martijn Wubs[a], Sanshui Xiao[a], Min Yan[a,b], Z. Fatih Öztürk[a,c], Antti-Pekka Jauho[d,e] and N. Asger Mortensen[a]

[a] DTU Fotonik, Department of Photonics Engineering, Technical University of Denmark, Ørsteds Plads, DK-2800 Kgs. Lyngby, Denmark;
[b] Laboratory of Photonics and Microwave Engineering, School of Information and Communication Technology, Royal Institute of Technology (KTH), Sweden;
[c] Istanbul Technical University, Istanbul, Turkey;
[d] Department of Applied Physics, Aalto University School of Science and Technology, P.O. Box 11100, FI-00076 Aalto, Finland;
[e] DTU Nanotech, Department of Micro- and Nanotechnology, Technical University of Denmark, Ørsteds Plads, DK-2800 Kgs. Lyngby, Denmark

ABSTRACT

We study the importance of taking the nonlocal optical response of metals into account for accurate determination of optical properties of nanoplasmonic structures. Here we focus on the computational physics aspects of this problem, and in particular we report on the nonlocal-response package that we wrote for state-of the art numerical software, enabling us to take into account the nonlocal material response of metals for any arbitrarily shaped nanoplasmonic structures, without much numerical overhead as compared to the standard local response. Our method is a frequency-domain method, and hence it is sensitive to possible narrow resonances that may arise due to strong electronic quantum confinement in the metal. This feature allows us to accurately determine which geometries are strongly affected by nonlocal response, for example regarding applications based on electric field enhancement properties for which metal nanostructures are widely used.

Keywords: Nanoplasmonics, nonlocal optical response, hydrodynamical Drude model, field enhancement

1. INTRODUCTION

One of the major reasons why plasmonics is currently so actively studied is the promise of miniaturization, through the ability of metal structures to spatially confine optical fields to sizes smaller than the optical wavelength (see, e.g.[1]). Another reason is the possibility of achieving huge enhancements of electric fields close to metal structures, especially for geometries with sharp features.[1] As the sizes of plasmonic structures are made ever smaller and geometries become sharper, at some point the description of the optical response of the metal by the bulk Drude response function will break down and new physics emerges. The usual Drude response describes how light interacts with the free conduction electrons of the metal, and an assumption that goes into this model is that the conduction electrons can be described as if they move collectively and scatter amongst each other in an infinite homogeneous medium. However, as metal structures become of dimensions much smaller than an optical wavelength, at some point the electrons start to "feel the walls" and to probe the geometry of the metal. A closely related issue is that the optical response of matter with moving charges should be described by a dielectric function that takes spatial dispersion into account.[2–5] This wave vector dependence of the dielectric function can safely be neglected for bulk matter, but it starts to become important for sub-wavelength plasmonic structures.

Effects of nonlocal response have been studied before,[6–8] but mainly for several simple geometries, such as planar interfaces,[2,9] (hollow) spheres,[10–12] and for metal nanowires.[4,13] However, there is a clear need for

Further author information: N.A.M.: E-mail: asger@mailaps.org, Telephone: +45 45256622; M. W.: E-mail: mwubs@fotonik.dtu.dk, Telephone: +45 45256574; G.T.: E-mail: gtos@fotonik.dtu.dk, Telephone: + 45 45253614

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versatile general numerical tools that do not depend on any symmetries in the geometries of the plasmonic structure.

In order to avoid confusion, remark that the nonlocal response that is the topic here is different from the nonlocal response discussed in recent "homogenization" literature on effective parameters of metamaterials, where an inhomogeneous metamaterial is described as an effective homogeneous medium, and the effective description may not be possible unless nonlocal response is allowed for, see for example the measurements and theory for nanorod metamaterials by Pollard *et al.*[14]

Our philosophy in implementing Maxwell's equations with nonlocal response has been to use well-tested standard commercial software as much as possible. The numerical work consisted of writing a nonlocal-response package as an add-on to standard commercial software (COMSOL), allowing fast and efficient determination of effects of nonlocal response for arbitrary plasmonic geometries. Depending on the parameters, large qualitative differences can be found between geometries with and without nonlocal response.

The structure of this paper is as follows: In Section 2 we briefly give a theoretical background of our numerical efforts. The main section is Section 3, in which we discuss the numerical implementation of the nonlocal-response calculation and present some benchmark calculations, to get an idea about the scaling of the required extra computational effort. Finally, Section 4 contains the summary, conclusions and outlook.

2. THEORETICAL BACKGROUND

Nonlocal response means that the relative dielectric function ε besides the usual frequency dispersion also has a wave-vector dependence, in other words the relation between the electric displacement and electric fields is given by

$$\mathbf{D}(\mathbf{k},\omega) = \varepsilon_0 \varepsilon(\mathbf{k},\omega)\mathbf{E}(\mathbf{k},\omega). \tag{1}$$

It is the wave vector dependence of the dielectric function that gives the nonlocal response, as we see below after transforming Eq. 1 to real space. But first recall that the standard, local dielectric function for metals has three components:

$$\varepsilon(\omega) = \varepsilon_\infty + \varepsilon_{\text{inter}}(\omega) + \varepsilon_{\text{intra}}(\omega), \tag{2}$$

with ε_∞ the value for infinite frequency, $\varepsilon_{\text{inter}}(\omega)$ is the contribution from the d-band electronic transitions, and $\varepsilon_{\text{intra}}(\omega)$ is due to excitation due to excitations of the conduction electrons. The last term is the free-electron term that is usually described by a Drude model,[15] leading to the following simple contribution to the total dielectric function:

$$\varepsilon_{\text{intra}}(\omega) = \varepsilon_{\text{D}}(\omega) = -\frac{\omega_p^2}{\omega(\omega + \mathrm{i}\gamma)}, \tag{3}$$

where ω_p is the plasma frequency of the metal, and the subscript D stands for 'Drude'. The above local-response model does not take into account the fact that conduction electrons move freely with typically the Fermi velocity in the metal, until their momentum changes due to collision processes as captured in the single Drude parameter γ. But it is the finite velocity that leads to a k-dependence of the Drude response function $\varepsilon(\mathbf{k},\omega)$. This k-dependence normally plays no observable role in bulk properties, as one can show, and is therefore usually left out. But as we shall see, it may have important effects in nanoplasmonics.

Although the model (3) has proved to be accurate enough for many situations, it is expected to be no longer accurate for very small (of order $\sim$ 10nm) metal nanostructures, where the size of the nanostructure is comparable to the mean free path of the conduction electrons. We will now slightly modify the Drude response function (3) so as to take nonlocal response into account:

$$\varepsilon_{\text{intra}}(\mathbf{k},\omega) = \varepsilon_{\text{D}}(\mathbf{k},\omega) = -\frac{\omega_p^2}{\omega(\omega + \mathrm{i}\gamma) - \beta^2 k^2}, \tag{4}$$

where β is related to the Fermi velocity, and depends on dimension of the geometry, and for example $\beta = v_{\text{F}}/\sqrt{2}$ for a free electron gas in 2D.[4] This corresponds to the hydrodynamical Drude model, and an excellent discussion of what goes into its derivation is given in the review by Pitarke *et al.*[2] This model is also used in the recent letter by McMahon *et al.*[4]

It should be remarked that more detailed and accurate models exist.[2,9] Those more refined models developed by solid-state physicists working on many-electron theory can be used by optic researchers at the expense of increased computation time, and not necessarily leading to additional insight. In that sense, our choice to work with the hydrodynamical Drude model is a compromise, but a useful one, since it allows one to calculate interesting optical effects due to quantum confinement in nanoplasmonic structures of arbitrary shape.[4]

Now we can proceed as in McMahon *et al.*[4] to go to a real-space description of the coupled dynamics between the optical electric field $\mathbf{E}$ and the electrons as captured in the "nonlocal phasor polarization current" $\mathbf{J}$.[4] However, our approach differs in an essential way from the numerical method introduced in,[4] in that we work in the frequency domain rather than in the time domain. We find that the effect on the electric field $\mathbf{E}(\mathbf{r},\omega)$ of the nonlocal material response can be found by solving the coupled equations of motion:

$$\left[\nabla\times\nabla\times-\varepsilon_1(\omega)\frac{\omega^2}{c^2}\right]\mathbf{E}(\mathbf{r},\omega) = \mathrm{i}\omega\mu_0\mathbf{J}(\mathbf{r},\omega), \tag{5a}$$

$$\left[\nabla^2+\frac{\omega(\omega+\mathrm{i}\gamma)}{\beta^2}\right]\mathbf{J}(\mathbf{r},\omega) = \frac{\mathrm{i}\varepsilon_0\omega_p^2\omega}{\beta^2}\,\mathbf{E}(\mathbf{r},\omega). \tag{5b}$$

As is clear from these equations, if the coupling parameters to the source-terms on the right-hand sides are small, then the magnitude of optical wave vectors is of the order of ω/c, whereas the magnitude of electronic wave vectors at the same frequency are given by ω/β (neglecting γ for the moment since it is $\ll\omega$). Since β is related to the Fermi velocity v_F and typically $v_\mathrm{F}=0.1c$, a (very) crude estimate gives that the electronic wave vectors are an order of magnitude larger than the optical wave vectors. In other words, electronic wave functions vary on a smaller scale than optical mode functions.

The above coupled equations (5a,5b) are the central equations for calculating nonlocal response. Eq 5a is a true vector wave equation for light, driven by the polarization current $\mathbf{J}$, whereas Eq. 5b latter is a compact notation for three scalar Helmholtz equations, one for every component of $\mathbf{J}$, with the electric field as a driving term. A difference between the two equations is that the light can travel in all of space, while the polarization current is associated with the plasmonic response of the metal only. Mathematically we need additional boundary conditions besides the usual ones for light to arrive at a unique solution of these coupled equations. The additional assumption that we will make, and which is the simplest and most common thing to do at this point, is to assume so-called Pekar boundary conditions. This simply means that we assume that $\mathbf{J}$ vanishes at the metal surface. This is a good assumption as long as we are not studying the hereby neglected quantum tunneling effects.

3. NUMERICAL IMPLEMENTATION

Now we proceed with the description of our numerical method for calculating nonlocal response. The code that implements Maxwell's equations with nonlocal response is written in the COMSOL MATLAB language. It consists of a modular code divided in two subprograms. The first subprogram performs the control tasks, and the second subprogram is the main frame which implements the system of equations (5a,5b). It has been tested on two UNIX machines equipped with Intel(R) Core(TM)2 Duo CPU E7200 and Dual-Core AMD Opteron(TM) Processor 2212 HE, and running linux kernel version 2.6.31 and 2.6.18 respectively.

The test geometry for this code was studying the behavior of an infinite long circular nanowire when a linearly polarized TE field directed along the rod axis incomes on it. The optical wavelength ($\approx$ 600nm) is much bigger than the dimension of the physical system ($\approx$ 10nm), but the simulations reveal that they strongly interact within each other in the non-local picture. The structure of this program is general, and it can be used for all kinds of waveguide geometries besides the circular nanowire.

The first subprogram is a BASH script that sets the most important parameters at the startup (see Figure 1, left part). These parameters include the radius of the nanorod, the dimensions of the simulation box, the flag to enable the non-local effects, the mesh size, the order of the interpolating polynomials, and the name of the output file. The bash script accesses the COMSOL MATLAB script before it starts, and it modifies the lines where these parameters are included by means of UNIX commands for string manipulation, such as *awk* and *cat*. The bash script launches the main program afterwards. This command is included in a *for* statement that

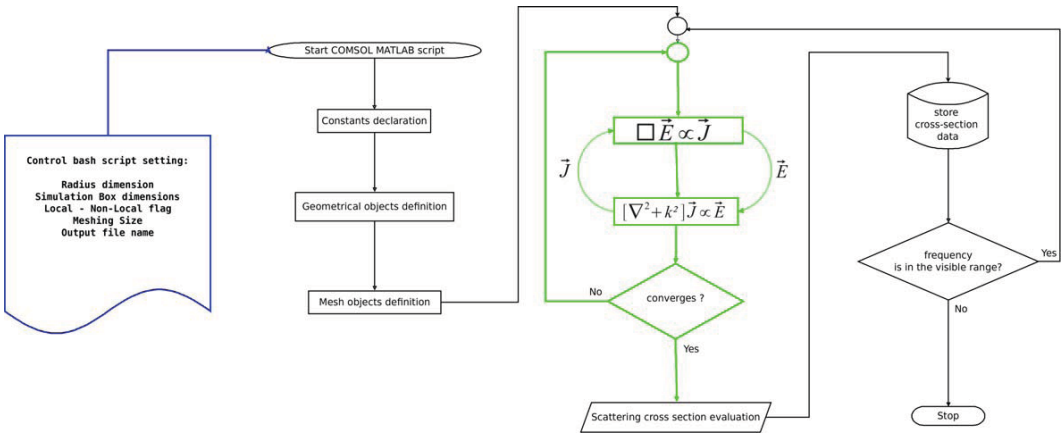

Figure 1. Flow diagram of the program discussed in the main text that calculates electromagnetic properties of plasmonic structures with nonlocal optical response.

varies the wire radius, and it can be activated when a parametric simulation is needed. Dividing the program into two subprograms makes the code both easier to read and run faster.

The main script (see Fig. 1 on the right) consists of five parts that perform the main tasks of a typical Frequency Domain Finite Element program. The first part contains the declaration of constants and global expressions.

The second part deals with the geometrical object definitions. Here a descriptive COMSOL language is used to draw the simulation box and the integration domains. In this case the simulation box is a square with PML boundary conditions at its external boundaries, to avoid electromagnetic waves to be reflected back by the walls. This box contains the geometric domain representing the physical system under test. The dimensions of the box can be varied in the bash script, in order to study systems at different scales.

The third part contains the commands that control the meshing properties of the integration domains. In particular, it is possible to change the size of the meshes or to create adaptive meshes.

The fourth part is the core of the program (shown in green in Fig. 1). Its main objective is calculating the scattering cross section of the metallic nanostructure under test at various frequencies. This is done by means of the external *for* cycle that runs over different frequencies in the visible range. This part contains the declaration of the governing equations in the various domain and of the boundary conditions. The TE wave equation model is already included in the RF Module library of COMSOL, and likewise the Helmholtz equation is included in the PDE models library. Usually one specifies the equations to be solved in the COMSOL modules in the familiar differential form. However, the program actually solves the equations plus boundary conditions after writing them in the integral form (or "weak form").[16] We found that we have to specify the equations in the weak form from the start, in order to be able to calculate nonlocal response with COMSOL. In more detail, the equations must be written in the weak form in order to add an inhomogeneous term to the wave equation for the electric field.

The coupling between the two equations in this cycle is implemented by means of an inner cycle where the equations are solved and the result is given as output if the solution converges. This cycle is automatically provided by COMSOL when running in multiphysics mode, so that you do not need to implement it at a low level. The outputs are the dependent variables of the system that in this case are given by the electric field, the magnetic field, the magnetic potential, the divergence condition variable, and the current density.

The fifth part deals with the postprocessing process. In this part the data coming from the previous data flow are processed and the scattering cross section is evaluated. This is implemented by performing the line integral of the normal component of the Poynting vector along a circular path enclosing our structure. The line integral calculation of a function is a useful command embedded in COMSOL.

Figure 2 shows the time it takes to do the computation as a function of the radius of the nanorod. The

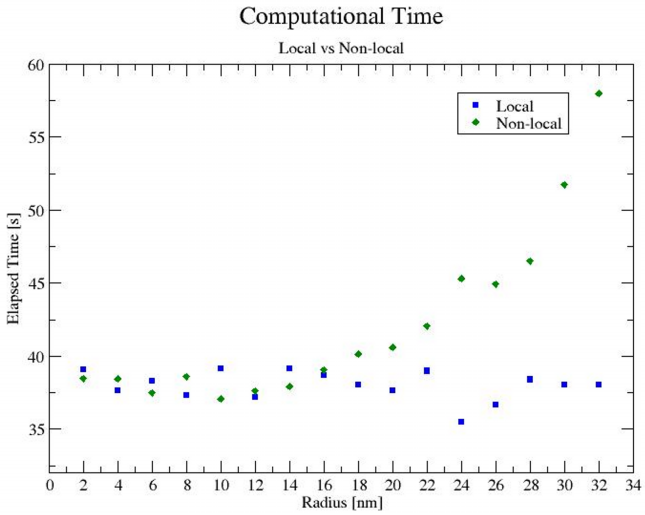

Figure 2. Comparison of the time to compute the current density in the nanowire with and without nonlocal response, as a function of the wire radius R.

simulations were run on the AMD processor mentioned earlier. The local and non-local case were compared. The main difference between the two models is that there are no coupled equations in the local model, so that the green loop in Fig. 1 is not accessed. The results show that the elapsed times are comparable for small structures ($2\text{nm} < R < 16\text{nm}$). As soon as the radius increases, the effect of the coupling equations becomes prominent and the computational time for the nonlocal case increases, whereas it remains essentially constant in the local model. The computational time is strongly affected by the number of points in the meshes, which affects the dimension of the FE matrix to be inverted. This causes some fluctuations in the values as can be observed in Fig. 2, because the meshes are automatically generated by COMSOL and they differ for each radius.

Figure 3 shows the current density in an $R = 2\,\text{nm}$ nanorod when excited with a perpendicular optical plane wave with energy 1.78eV. The local model shows no resonance in the structure, whereas the the non-local structure exhibits a strong resonance.

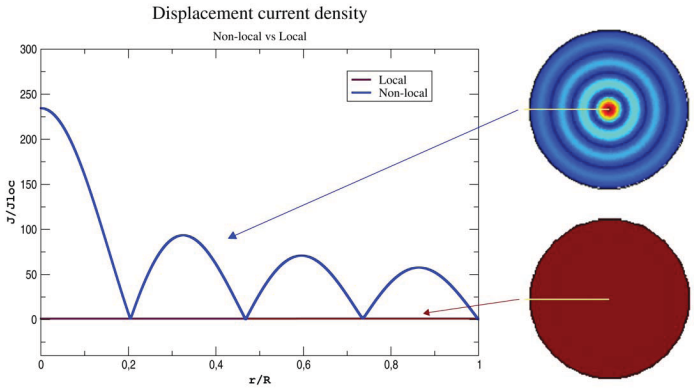

Figure 3. Current densities in a nanowire of radius 2nm when excited by a plane wave of 3.81 eV, with and without nonlocal response included.

4. CONCLUSIONS, OUTLOOK AND DISCUSSION

In summary, we have studied the nonlocal optical response of small nanoplasmonic structures. We presented our implementation of the numerical evaluation of the optical properties due to nonlocal response, and hope that this will beneficial for colleagues embarking on similar explorations. Furthermore, it was shown that taking nonlocal response into account gives rise to longer calculation times. For the wire geometry considered here, the calculations are fast, on the order of a minute, but for more complex geometries further optimization may be required. We showed the first results of the comparison between optical fields in the presence of only local material response as compared to both local and nonlocal response. Since the differences can be substantial, especially for small structures much smaller than optical wavelengths, this shows that the usual Drude bulk description of metals breaks down.

Although the hydrodynamical Drude model that we employ is more accurate that the usual Drude bulk model and we anticipate that it will predict several new observable phenomena in nanoplasmonics, it has its limitations as well. The most obvious limitation is that additional boundary conditions need to be chosen, and our choice of Pekar boundary conditions by definition excludes electronic quantum tunneling phenomena from the model. We think this is an excellent approximation, unless one is interested in quantum tunneling itself and the optical field that it generates.

After implementation of our method to calculate nonlocal optical response, a whole new class of problems can be explored. For since our method is general, one is in the position to study arbitrary plasmonic structures with it, and in the near future we plan to use our method to explore several other geometries of interest. One area of research for which our work may become relevant is quantum plasmonics.[17–20] We also intend to use our numerical method together with analytical calculations to get more insight when and where nonlocal response will significantly alter the optical fields.

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