Challenges In Simulation Of Optical Properties Of Metallic Nanoparticles Using The Discrete Dipole Approximation

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Abstract. I discuss the accuracy and computational time of the discrete dipole approximation (DDA) when applied to metal nanoparticles. The accuracy of the DDA can be made satisfactory by refining discretization (or increasing number of dipoles), but the required discretization level strongly depends on particle shape and refractive index (or wavelength) as well as on a particular computed quantity of interest. I present certain guidelines for setting the appropriate discretization, but they can not be considered comprehensive. On contrary, the required computational time can be accurately estimated once the number of dipoles is set. For that approximate expression for the required number of iterations of the iterative solver is used, which validity was tested for a wide range of refractive index.

Keywords: discrete dipole approximation, metal nanoparticles, numerical simulation.
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INTRODUCTION

The discrete dipole approximation (DDA) is a general method to simulate light scattering by particles of arbitrary size, shape, and composition [1–3]. Due to its versatility and availability of efficient publicly available codes [4,5] the DDA is widely used for simulation of optical properties of nanoparticles in different configurations, including single, on surface [6], periodic arrays [7], and even more complex combinations [8]. However, apparent ease-of-use has led many researchers to use the DDA as a black box with little regard for either its internal parameters or the final accuracy of computed optical quantities.

The goal of this contribution is to discuss the internal working of the DDA and existing challenges of its application to metallic nanoparticles. In particular, I focus on two related aspects: accuracy and computational time. It is partly based on recently published results [9,10] but also contains new data and conclusions.

ACCURACY

The agreement between the DDA simulations and experiments has never been perfect. However, it is usually attributed to uncertainty in particle morphology and complex refractive index m. The accuracy of the DDA itself is usually implicitly assumed good enough based on a long history of this method. Unfortunately, this assumption can be erroneous [9]. On the one hand, the DDA is numerically exact method in the sense that its accuracy can be made as good as required by refining particle volume discretization given sufficient computer power [11]. On the other hand, any practical usage of the DDA involves a certain discretization level (leading to finite error) that is usually chosen *a priori*. The problem is that the DDA was originally developed for astrophysical applications [1,2], and its accuracy was mostly studied for m near range from 1 to 3 on the real axis. Corresponding conclusions about sufficient discretization level are usually extrapolated to the plasmonic refractive indices (see Figure 1) without verification. Moreover, there is little interaction between developers of the DDA and corresponding codes and those that use it in plasmonic applications.

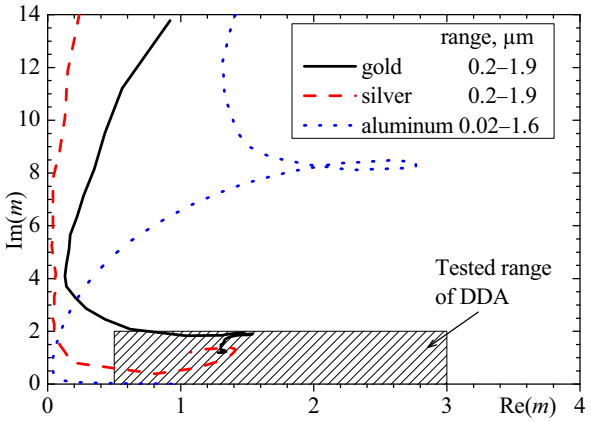

FIGURE 1. Refractive indices of gold, silver [13], and aluminium [14] in wide spectral ranges. Well-tested range of the DDA is schematically depicted for comparison.

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The accuracy of the DDA for gold nanoparticles was recently studied through extensive simulations varying the discretization level [9]. Moreover, apart from the standard lattice-dispersion-relation (LDR) formulation of the DDA, the less-common filtered coupled dipoles (FCD, [12]) was tested. The main conclusion of that study is that the discretization, required for a satisfactory accuracy, varies a lot depending on particle shape and particular computed quantity of interest. For instance, the DDA successfully predicts position and amplitudes of spectral peaks, using moderate discretization (32 dipoles per shortest particle dimension). However, a much finer discretization (4-8 smaller dipole size) is required to keep the relative error of absorption efficiency Q_{abs} in the wavelength range [600,800] nm within 10%. The latter applies to spherical and rod-shaped particles, while the errors for the cubes are an order of magnitude smaller.

To generalize this study to other metals and outer media (e.g. water) note that the accuracy of the DDA (for a fixed discretization) depends largely on m and only weakly on size parameter $x = 2\pi r/\lambda$ (λ – wavelength, r – particle radius), especially when $x < 1$. Thus the dependence of accuracy on λ is almost equivalent to dependence on m for a fixed x. Example of the latter is shown in Figure 2. In particular, the most problematic values of m are that near imaginary axis, especially for imaginary parts from 0 to 4. Thus inaccuracy of the DDA for silver and aluminium can be even more pronounced than that for gold.

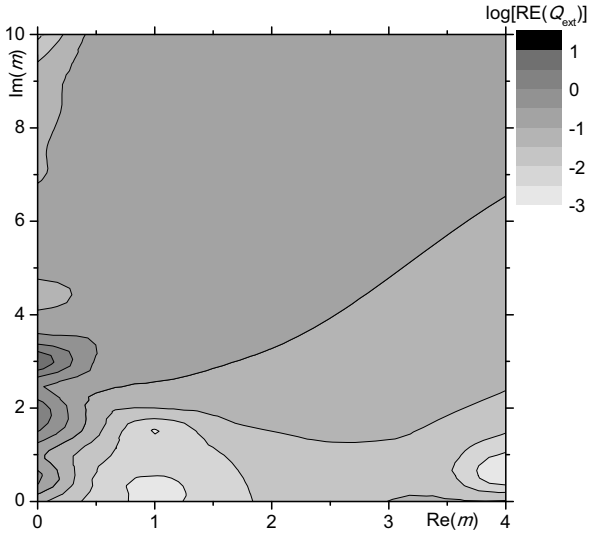

FIGURE 2. Contour plot of relative DDA errors (in logarithmic scale) for Q_{ext} of sphere with $x = 0.5$ versus m. DDA results are obtained using ADDA v.0.79 [5] using FCD formulation, 32 dipoles per sphere diameter, and step of 0.5 in both real and imaginary part of m (extrapolated between).

Nevertheless, due to large number of problem parameters it is hard to provide universal guidelines on sufficient discretization level. Therefore, an accuracy study of DDA for a particular application is advised to achieve a compromise between computational speed and accuracy of a specific quantity of interest.

COMPUTATIONAL TIME

Computation time of the DDA is mainly determined by the iterative solution of the large linear system [5]. Using FFT acceleration, the time of one iteration is O(Nln$N$), where N is number of dipoles used to discretize the particle. The latter is determined by the particular scattering problem and required accuracy, as discussed in the previous section. On contrary, number of iterations N_{iter} is almost independent on N and x (the latter when $x < 1$). Hence, it is determined mostly by m and particle shape. Moreover, it was shown [10] that for $x < 1$ particle shape has little influence on N_{iter} and the following approximate formula was derived:

$$N_{\text{iter}} \approx \frac{5\ln 10}{\ln\left|(m+1)/(m-1)\right|}, \qquad (1)$$

based on 10^{-5} convergence threshold. The accuracy of this formula was tested against DDA simulations for gold spheres for λ from 0.4 to 0.8 μm, showing agreement within a factor of two [10].

Here we test Equation (1) over a wider range of m and present results in Figure 3. One can see perfect qualitative agreement between the real and approximated results, except for the neighborhood of the imaginary axis. This difference is connected to the

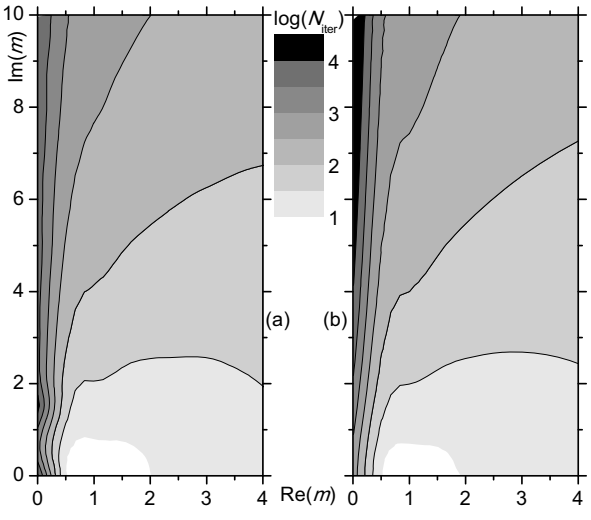

FIGURE 3. Contour plot of N_{iter} (in logarithmic scale) versus m: (a) actual DDA results with the same parameters as in Figure 2 and (b) calculated by Equation (1).

eigenvalue spectrum of the integral scattering operator, which depends on particle shape (see e.g. [12]). Generally, this spectrum spans over the whole positive imaginary axis in m-space. However, for a sphere it is concentrated into a single pole at $m = \mathrm{i}\sqrt{2}$. Therefore, the actual values of N_{iter} [Figure 3(a)] are larger than the estimate around this pole, but smaller for the rest of the imaginary axis. Quantitative comparison of data behind Figure 3 shows that apart for the imaginary axis Equation (1) is accurate within 20%.

Another useful implication of Equation (1) is the limiting value on N_{iter} for any particular metal at infra-red wavelengths. Using the Drude model (with standard parameters τ and ω_{p}), it was shown [10] that

$$1/\tau \ll \omega \ll \omega_{\mathrm{p}} \Rightarrow N_{\mathrm{iter}}(\omega) \approx 5\omega_{\mathrm{p}}\tau \ln 10\,, \qquad (2)$$

which leads to values of about 10^3 for gold and aluminium and 5×10^3 for silver. For shorter wavelengths N_{iter} is smaller.

CONCLUSION

The discrete dipole approximation is perfectly suitable for accurate simulation of optical properties of metal nanoparticles. However, it should be used with caution, especially regarding the discretization level. Certain general guidelines are given in this contribution. In particular, accuracy of the DDA for silver is generally worse than for gold. However, it is hard to predict the required discretization *a priori*. Therefore, it is recommended to perform an accuracy study for a particular application.

After the appropriate discretization level is determined, required computational time can be accurately estimated. For that approximate expression for the required number of iterations of the iterative solver is used, which validity was tested for the range of refractive index typical for metals for visible and near-infra-red wavelengths. It was shown that the number of iterations should not exceed several thousands.

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