Abstract.
The discrete dipole approximation (DDA) allows one to simulate interaction of light with particles of arbitrary shape and structure. We performed theoretical development of the method, including estimate of the simulation accuracy, and developed a parallel computer code. These advances were used to study the DDA accuracy for gold nanoparticles. We showed that new DDA formulation (filtered coupled dipoles) significantly increases both accuracy and speed of simulations.

Introduction.

Plasmon resonance in metal nanoparticles has gained increasing interest in recent years [1,2]. Applications of these nanoparticles are based on their ability to concentrate electromagnetic energy into subwavelength regions and include surface-enhanced Raman scattering and fluorescence. Development in this field is pushed by many different methods to produce nanoparticles of different size, shape, and composition, based on chemical synthesis or nanolithography.

Simulation of interaction of light with nanoparticles is an important part of the scientific progress in this field [2,3]. It is used both to validate existing nanostructures and to aid design of new ones with specific properties. Several methods can be used for particles of arbitrary shapes, in particular, the DDA [4,5]. It is widely used for simulation of optical properties of metallic nanoparticles, due to its versatility and public availability of efficient computer implementations.

Agreement between the DDA simulations and experiments for extinction spectra of gold (as well, as other metallic) nanoparticles has never been perfect [4,6]. However, the disagreement is attributed mostly to uncertainties in particle shape [6] and in the gold refractive index [4]. The accuracy of the DDA itself for these problems is usually quoted as "good enough if a large enough number of dipoles is used", i.e. the discussion is qualitative with no error measurements available. Therewith, the errors of extinction efficiency at particular wavelengths can be as large as 50%.

This contribution reviews our recent progress in the theoretical development of the DDA, its implementation as a parallel computer code, and its application to simulate light scattering by gold nanoparticles.

Theoretical development of the DDA.

We performed a rigorous theoretical analysis of convergence of different DDA formulations [7]. Based on it we proposed an extrapolation technique to increase accuracy and to estimate the simulation errors [8]. The latter do not require comparison with other simulation methods. Hence, it can be used to build an adaptive algorithm to reach a prescribed accuracy at the least computational costs. Moreover, internal error estimates significantly improves the reliability of DDA results for particles, which do not allow an exact reference solution. We have also developed a special modification of the DDA for particles much smaller than the wavelength, which allows rapid simulation of the whole extinction spectrum [9].

Based on these theoretical results we performed an extensive review of the DDA, discussing both history of the method and recent advances using the same framework based on the integral equation for the electric field [10]. In this review numerical aspects of the DDA were also covered, since they are important for practical application of the method. Moreover, directions of further DDA development were proposed.

Computer implementation of the DDA and comparison with other codes.

We developed computer code "ADDA", capable to simulate light scattering by arbitrary particles. Its key feature is parallel execution on a computer cluster [11]. This allows, on one hand, to simulate light scattering by particles much larger than the wavelength and, on the other hand, to simulate particles comparable with or smaller than the wavelength with a high accuracy. This code is freely available and is continually developed (http://code.google.com/p/a-dda/). Currently, it is used by more than 50 researchers worldwide. An independent comparison showed that "ADDA" outperforms analogous codes in computational efficiency [12].

Reliability of this code was proven by comparison with two independent methods. First, we performed a systematic comparison of the DDA with the finite-difference time-domain method. The former was shown to be an order of magnitude faster for biological cells, while the latter is faster for refractive indices 1.7 and 2 [13]. Second, the DDA was compared to the discrete sources method for simulation of light scattering by red blood cells [14].

Accuracy of the DDA for gold nanoparticles.

We performed a systematic study of the DDA accuracy for gold nanoparticles [15]. We chose three particle shapes (a sphere, a cube, and a rod) and two sizes (10-100 nm) and computed absorption and scattering spectra, using a range of discretizations (number of dipoles) and two DDA formulations: lattice dispersion relation (LDR, [16]) and filtered coupled dipoles (FCD, [17]). The latter formulation was recently implemented in the "ADDA" code, and it was shown to be generally superior to the standard LDR [18].

Study [15] showed that in certain cases errors for gold nanoparticles can be unexpectedly large, while accurate results can be obtained only at expense of large computational time. The FCD formulation led to significantly more accurate results than the LDR, and is thus recommended for DDA simulations of optical properties of gold nanoparticles.

Conclusion.

We significantly advanced a theoretical base of the DDA and developed an efficient computer code, resulting in a reliable instrument for simulation of light scattering by particles of arbitrary shape and structure. The latter allowed us to study the DDA accuracy for gold nanoparticles in details and to formulate practical conclusions for this field. In particular, we recommended using a new DDA formulation (the FCD).

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