Electron-energy-loss spectroscopy and cathodoluminescence for particles inside substrate

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Abstract. To simulate the interaction of a nanoparticle with an electron beam, we previously developed a theoretical description for the general case of a particle fully embedded in an infinite arbitrary host medium. The theory is based on the volume-integral variant of frequency-domain Maxwell’s equations and, therefore, is naturally applicable in the discrete-dipole approximation. The fully-embedded approach allows fast numerical simulations of the experiments for particles inside a substrate since the host medium discretization is not needed. In this work, we study how applicable the fully-embedded approach is for realistic scenarios with relatively thin substrates. In particular, we performed test simulations for a silver sphere both inside an infinite host medium and inside a finite box or sphere. For the host medium, we considered two non-absorbing cases (the denser one causes Cherenkov radiation), as well as an absorbing case. The peak positions in the obtained spectra approximately agree between substrates a few times thicker than the sphere and the infinite one. However, a much thicker substrate (of the order of $\mu$m) would be required to have a qualitative agreement for absolute peak amplitudes. The developed algorithm is implemented in the open-source code ADDA, allowing one to rigorously and efficiently simulate electron-energy-loss spectroscopy and cathodoluminescence by particles of arbitrary shape and internal structure embedded into any homogeneous host medium.

1. Introduction
Electron microscopy is an advanced experimental technique used particularly for studying the optical properties of plasmonic nanoparticles. Optical methods can only excite “bright” plasmonic modes, and the diffraction limit confines their spatial resolution. By contrast, electron microscopy excites both “bright” and “dark” plasmonic modes and has a spatial resolution less than 1 nm and energy resolution less than 0.2 eV [1]. In the experiments, relativistic electrons interacting with a particle lose energy (electron-energy-loss spectroscopy – EELS) and the particle emits light (cathodoluminescence – CL). For each position of the electron beam concerning the particle, EELS and CL spectra are obtained. To accurately interpret the data, a computer simulation of the experiment is required.

The discrete dipole approximation (DDA) is a numerically exact method for simulating the interaction of the electro-magnetic field with particles of arbitrary shape and internal structure [2]. Previous implementations of EELS and CL in the DDA [3–5] are suitable only for interaction in a vacuum when only a particle and an electron are present. However, in actual experiments, the particle is commonly placed onto (or inside) a substrate to resist gravitation and collisions with fast electrons. We previously derived a theory [6] for the general case of an arbitrary infinite host medium (refractive
index $m_n$) even absorbing one or the one with the speed of electron exceeding that of light (Cherenkov radiation case). Moreover, this theory has been implemented in the open-source software ADDA [7].

This theory and simulation method are naturally applicable to particles inside a substrate (if the latter is large enough), but this has never been discussed in the literature except for a few cases of the most trivial (non-Cherenkov) host medium [8,9]. This work aims to study the effect of the host medium on the EELS and CL spectra. We compare the simulations for a particle fully-embedded into an infinite host medium to the same particle inside a finite box (or a sphere). The particle inside a finite medium is sometimes used as an approximation for the infinite host medium. However, it is computationally inefficient since the finite chunk of the host medium needs to be explicitly discretized. Nevertheless, in other applications, the host medium is limited (at least in one dimension). One would like to know whether the infinite-host-medium simulation would be accurate enough for this case.

2. Substrate simulation methods

In the comparisons, we use an electron with the 120 keV energy (the corresponding speed is $0.59c$, where $c$ is the speed of light in vacuum) and a silver 15-nm-radius sphere as a test particle. We apply three approaches to account for the medium: fully-embedded (new theory), a sphere in a box (“spherebox” shape in ADDA), and a coated sphere (“coated” shape in ADDA) (Figure 1).

In the fully-embedded case (Figure 1, a), the sphere is discretized with the 30x30x30 dipoles grid. In both spherebox (Figure 1, b) and coated (Figure 1, c) cases, the resulting particle is twice the size of the silver sphere and is discretized with a 60x60x60 dipoles grid. The latter discretization means that the silver sphere itself is discretized with the same 30x30x30 dipoles grid as in the embedded case, while additional dipoles are used to discretize the surrounding medium. All simulations are performed using ADDA, optical properties for silver are taken from [10].

![Figure 1](gid00076)  
Figure 1. Silver sphere inside host media with the refractive index $m_n$. a) Fully-embedded into the infinite host medium. b) Inside a larger cube. c) Inside a larger sphere.

3. Results and discussion

First, we tested the accuracy of ADDA by comparing simulation results to the reference Lorenz-Mie [11] solution for the sphere in a vacuum ($m_n = 1$) (Figure 2). Simulated spectra were close to the exact solution; the error of the peak position (3.5 eV) was only 0.05 eV. Further improvement could be obtained by increasing the discretization level or using Richardson extrapolation [12].
Figure 2. EELS (a) and CL (b) spectra in vacuum ($m_h = 1$) simulated with the DDA and the Lorenz-Mie theory.

EELS and CL spectra are shown for the particle in a non-absorbing host medium ($m_h = 1.5$) (Figure 3) when the electron's speed is lower than the speed of light in the medium ($0.67c$). All three peaks were shifted to the lower energy (2.9 eV). Additionally, the peak in the infinite host medium had a much smaller amplitude.

Figure 3. EELS (a) and CL (b) spectra for the case of $m_h = 1.5$, simulated with the DDA. Geometries are shown in Figure 1.

EELS and CL spectra are shown (Figure 4) for the particle in the host medium with $m_h = 2$ leading to the Cherenkov radiation since the electron's speed was greater than the speed of light in the medium ($0.5c$). Compared to the case of $m_h = 1.5$, the peaks were shifted to even lower energy (2.4 eV), but their positions remained similar for all geometries. The peak amplitude for the embedded case was further reduced, while it even increased for finite-medium. The latter can be due to the Cherenkov radiation, which is effectively accounted for in these geometries but should be added separately in the embedded case. While there is a simple Frank–Tamm formula for Cherenkov losses in a sufficiently large chunk of host medium, the studied finite systems are too small for the formula’s applicability. We expect the formula to be applicable at a box size of one or several μm, depending on particular loss energy (the size should be at least several corresponding wavelengths). However, the peak position is determined by the local environment of the silver sphere and is expected to converge to the infinite-medium result for box sizes only several times larger than the sphere diameter. We will present more simulations at the conference to support this hypothesis.
Figure 4. Same as Figure 3, but for $m_b = 2$ (Cherenkov case).

For the absorbing host medium, the proper way to define CL remains an open question, so we only show the results for EELS in Figure 5. The introduced absorption did not significantly change the peak positions, determined by the real part of the refractive index (3.5 and 2.9 eV, respectively). The differences in peak amplitude result partly from the intrinsic absorption in the host medium, unaccounted for in the embedded (similar to the Cherenkov case).

Figure 5. EELS spectra in absorbing host medium, (a) $m_b = 1 + 0.1i$ and (b) $m_b = 1.5 + 0.1i$ simulated with the DDA. Geometries are shown in Figure 1.

4. Conclusion
We introduced the “embedded into the host medium” approach for simulating EELS and CL in the DDA. This approach allows more efficient calculations for EELS and CL experiments for particles inside substrate than the old-fashioned way of discretizing the surrounding medium. Test simulations for a silver sphere show that the peak positions in the obtained spectra approximately reproduce the experimental for substrates several times thicker than the sphere.

A much thicker substrate (at least 1 μm) is required to have a qualitative agreement for absolute peak amplitudes. The latter would also require manual accounting for losses in the host medium if it is absorbing or sufficiently dense to cause Cherenkov radiation. These new capabilities for simulating EELS and CL are available at https://github.com/alkichigin/adda and will be implemented in the next official ADDA release.

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