



2014 BioNanotechnology Summer Institute

Cancer Nanotechnology and Cell Mechanics

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University of Illinois at Urbana-Champaign



NANO-OPTICS MODULE

Discrete Dipole Approximation (DDA) Simulation of Scattering and Absorption of Metal Nanoparticles

Location: 1000 MNTL

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Lab Assistants: Jeremy Smith, Chemical Physics, and Sarah White, Chemistry

Purpose

The purpose of this lab module is to provide experience using the discrete dipole approximation (DDA) to simulate the interaction of metal nanoparticles with the electric field of incident light and use this computational method to produce the scattering and absorption spectra of metal nanoparticles as a function of size, geometry, and medium. The goal is to equip students with a method for predictive design of optical properties of metal nanoparticles for their use in biological and medical applications.

Background

The strongly enhanced surface plasmon resonance of noble metal nanoparticles at optical frequencies makes them excellent scatterers and absorbers of physical light. Superior optical properties, coupled with recent advances in nanoparticle synthesis, conjugation, and assembly, have stimulated interest in the use of plasmon-resonant nanoparticles and nanostructures for optical and photonic applications and, more recently, for biomedical applications. Nanoparticles composed of gold offer, in addition to their enhanced absorption and scattering, good biocompatibility, facile synthesis, and conjugation to a variety of biomolecular ligands, antibodies, and other targeting moieties, making them suitable for use in biochemical sensing and detection, medical diagnostics, and therapeutic applications. There have been several demonstrations of bioaffinity sensors based on the plasmon absorption and scattering of nanoparticles and their assemblies.

Another notable use of gold nanoparticles has been as contrast agents in cellular and biological imaging. Contrast agents in medical and biological imaging improve the sensitivity and diagnostic ability of the imaging modality by site-specifically labeling tissues or cells of interest. The effectiveness of nanoparticles as biomedical imaging contrast and therapeutic agents depends on their optical properties. For instance, a high-scattering cross-section is essential for cell imaging applications based on light-scattering microscopy. On the other hand, effective photothermal therapy with minimal laser dosage requires a high nanoparticle absorption cross-section with low scattering losses. Biosensing applications based on surface plasmon resonance shifts necessitate strong resonance in the wavelength sensitivity range of the instrument as well as narrow optical resonance line widths. For actual in vivo imaging and therapeutic applications, the optical resonance of the nanoparticles is strongly desired to be in the near-infrared (NIR) region of the biological water window, where the tissue transmissivity is the highest. In addition, the nanoparticle size is also an important consideration for nanoparticle uptake and retention by cells and tissue.

It is well-known that the plasmon resonance of metal nanoparticles is strongly sensitive to the nanoparticle size, shape, and the dielectric properties of the surrounding medium. Optical properties of gold nanoparticles can thus be readily tuned by varying their size and shape. In order to harness the full power of these phenomena, scientists need to understand the interactions of light with nanoparticles at very small length scales. There have been several experimental reports on the optical properties of metal nanoparticles, including gold nanospheres, nanorods, and nanoprisms, silver nanospheres, nanowires, and nanoprisms, copper nanospheres, aluminum nanospheres, bimetallic nanoparticles, composite nanoparticles with a core-shell structure, and nanoparticle chains and assemblies. At the same time, well-established theoretical tools based on the Mie theory and the discrete dipole approximation (DDA) method have been readily exploited for a quantitative study of the nanoparticle optical properties of different size, shape, composition, and aggregation state, etc.

DDA is a very powerful method for determining the interaction of electromagnetic radiation with particles. Using DDA, the particle is discretized into an array of dipoles, or polarizable points. This method then solves Maxwell's equations for an incident field interacting with each of the dipoles individually. The resulting data can be used to compute scattering and absorption properties of the array of dipoles and, hence, the particle. This method relies on the assumption that the dielectric properties of the particle, and its interaction with the incident field, are directly related to the polarizability of the constituent dipoles.

A popular code for the implementation of DDA calculations is called DDSCAT. DDSCAT allows for the computation of absorption and scattering properties of particles with arbitrary shapes and geometries, and provides outputs of light extinction, absorption, and scattering properties at various wavelengths of incident light.

The nanobioNODE at University of Illinois has developed a tool on nanoHUB.org that creates a simple and intuitive interface for using the DDSCAT code developed by Draine and Flatau. This allows experimental chemists and biologist not familiar with computational methods a visual interface in which they can simulate the interaction of light with nanoparticles of any geometry and compute light scattering, absorption, and plasmonic near field enhancement.

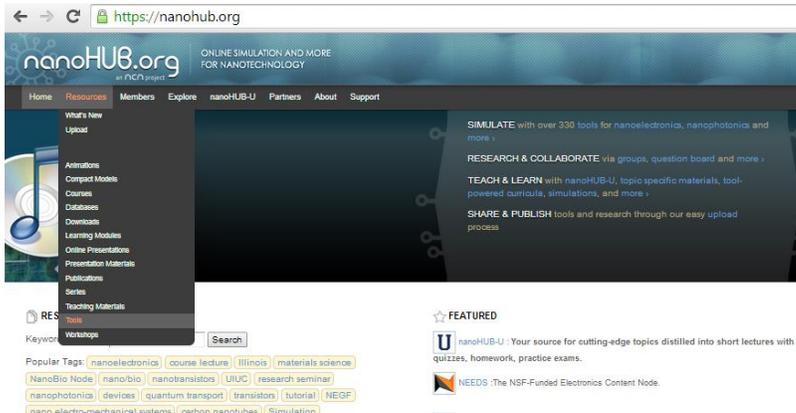
References

- Draine, Bruce T., and Piotr J. Flatau. "Discrete-dipole Approximation for Scattering Calculations." *Journal of the Optical Society of America A* 11.4 (1994): 1491. Web. (pdf)
- Draine, Bruce T., and Piotr J. Flatau. *User Guide for the Discrete Dipole Approximation Code DDSCAT 7.2*. N.p., 2012. Web.
- Jain, Prashant K., Kyeong Seok Lee, Ivan H. El-Sayed, and Mostafa A. El-Sayed. "Calculated Absorption and Scattering Properties of Gold Nanoparticles of Different Size, Shape, and Composition: Applications in Biological Imaging and Biomedicine." *The Journal of Physical Chemistry B* 110.14 (2006): 7238-248.
- Jain, Prashant K. "Plasmons in assembled metal nanostructures: radiative and nonradiative properties, near-field coupling and its universal scaling behavior." (2008).

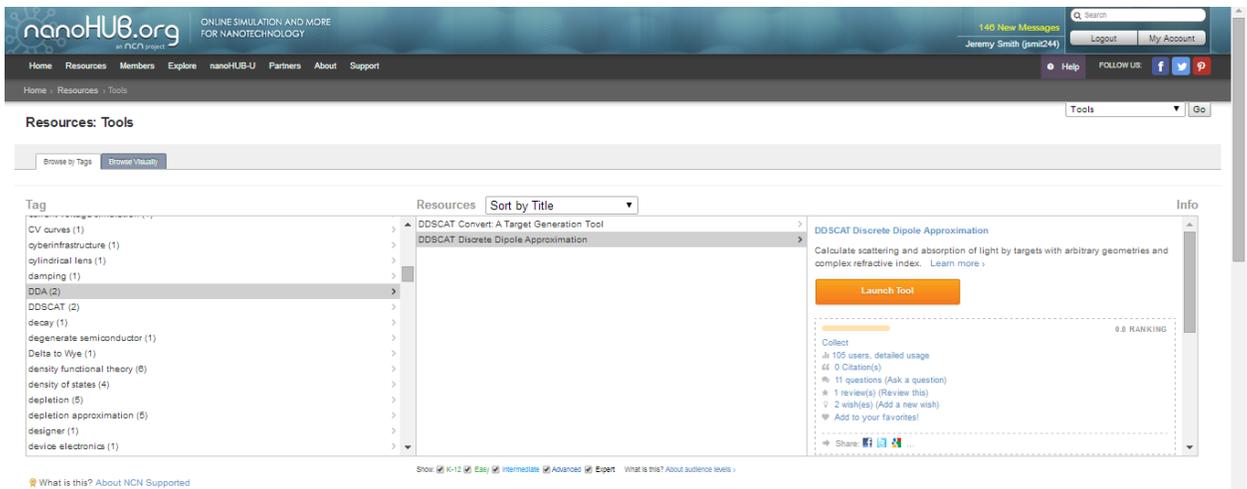
Running a Simulation

Generating and running a simple target shape file

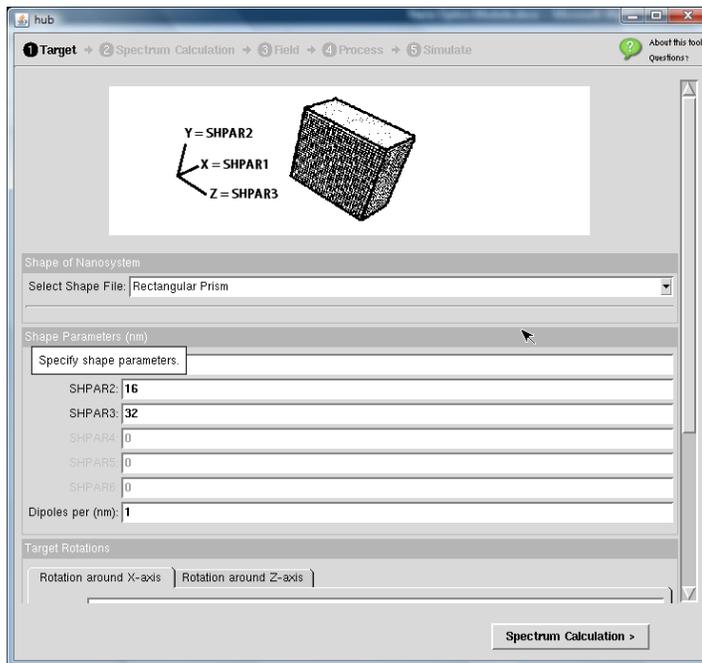
- 1) Log onto nanohub.org. You can either create a login to save your jobs for future reference, or login as a guest.



- 2) Go to the resources tab and click on Tools. From the list on the left scroll down to DDA. From the central list select DDSCAT discrete dipole approximation. On the right hand list click launch tool.

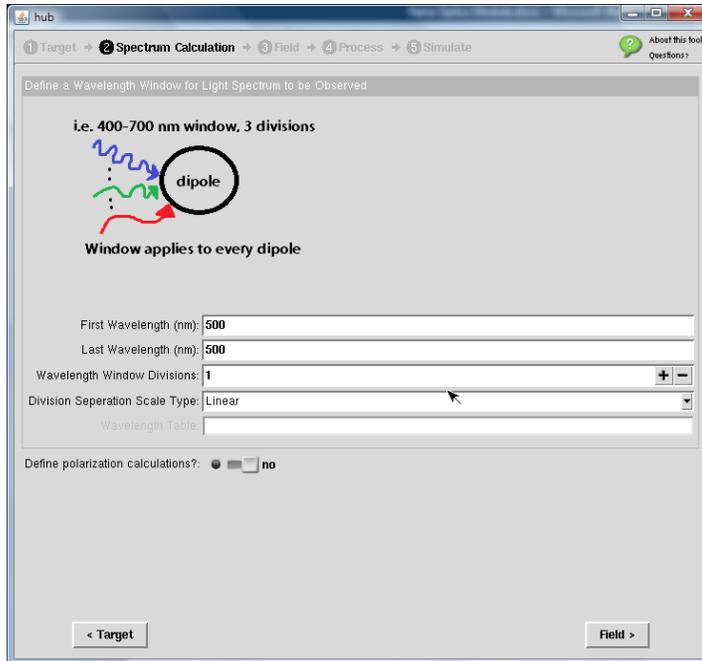


- 3) Now you have opened the DDA tool on Nanohub which will perform the calculation for you. We must go through a number steps to correctly setup the calculation. The first window is to specify the object, calculation resolution, medium and light polarization relative to the object.

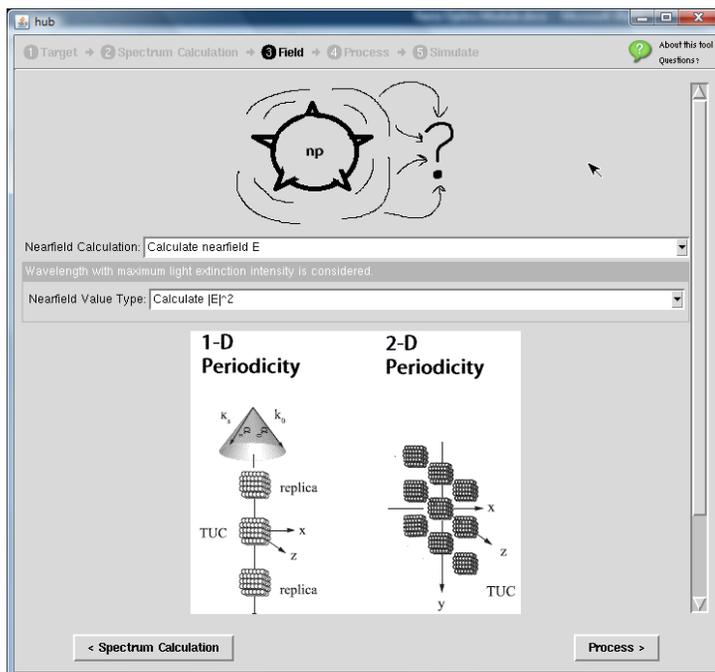


To start we will use built in shapes to motivate and understanding of the way the calculation is performed and the effect of important parameters on the spectra and electric field distribution. Under the shape file tab, select ellipsoid. In the three rows of the SHPAR dialogue box select 10,10 and 10 (nm). This will build a 10 nm sphere. In the dipole per nm bow enter 1. This defines the resolution of the calculation. Decreasing this number will describe a more accurate calculation, however it will take much longer, since the calculation scales as the (number of dipoles)². The target rotations tab allows one to rotate the object relative to the incident light. By default, the light propagates along the x direction. Since the light is fixed, rotating the object will change the angle between the electric field vector of the light and the object, and thus change the types of “modes” which are excited by the light. In the dielectric tab select 1 dielectric and select the material as Au. A materials dielectric function is a frequency (wavelength) dependent function that defines the response of a material to electromagnetic radiation. It essentially defines everything about the inherent response of a material in the absence of any particular geometry and what makes one material different from another (in terms of its response to light). Set the medium refractive index to 1.33 (water). Move to the next tab.

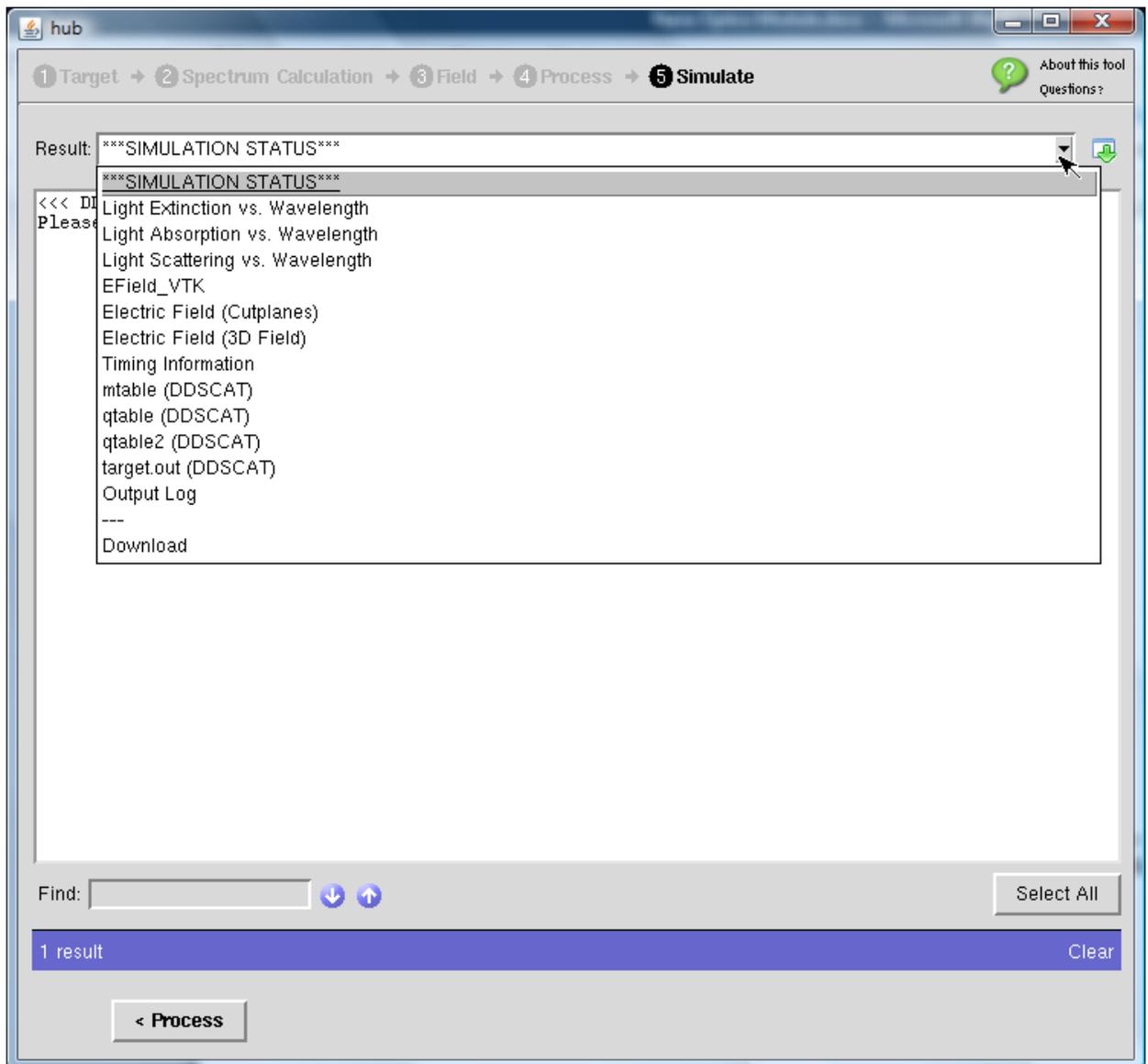
- 4) The second tab is where we specify how many division we want to use to calculate the spectrum of the object. Choose 500 to 600 nm, in 10 divisions. It is known from experiments that the plasmon resonance of a Au sphere should lie somewhere in this range. Changing the shape may require one to change the wavelength range to perform the calculation. Select define polarization in order to change the light polarization. By default the calculation sets the (electric field, recall light has perpendicular electric and magnetic fields) polarization along the y axis.



- 5) In the field tab, select calculate nearfield E, then select E^2 . This will calculate the field in the vicinity of the particle (or rather its magnitude, since we chose E^2).



- 6) In the process tab select local ddsat. This will use one process to perform the calculation. The tool is supported for performing calculations on a large cluster, which is desirable when we want to calculate large shapes, high resolution or many wavelengths. For the homework assignment you should select remote parallel DDSCAT, since the arbitrary geometry you will generate will likely take longer to run (and be performed over a large set of wavelengths).
- 7) The calculation should run in a matter of seconds. In the result tab there will be several files which you can look at and download. Absorption and scattering represent the absorption and scattering spectra respectively. Extinction is the sum of both of these. Download and save all three of these files. For fun you can click on the electric field cutplanes tab. This will plot the electric field in the vicinity of the object. This is by default at the maximum of the extinction spectrum. This will clearly illustrate the predominantly dipole nature of the observed resonance at $\lambda \approx 530$ nm.



Exercises

Size Dependence

Repeat the above procedure with Au spheres of sizes 20, 30, 40, 50 and 60 nm. Plot the resonance maximum, peak absorption, and peak scattering cross-section (m^2) as a function of size. How does the absolute and relative magnitude of absorption and scattering change as a function of size? What is the physical reason for this dependence? What are the implications for biomedical applications? (Hint: Imaging vs photothermal therapy). (see *J. Phys. Chem. B*, **2006**, *110* (14), pp 7238–7248).

Plasmon Modes of Anisotropic Nanoparticles

In the first tab of the DDA tool, (see above part 3) change the shape of the ellipsoid such that it is anisotropic. Namely, set SHPAR 1 and 2 = 5 nm and SHPAR 3 = 20 nm. This will elongate the shape along one axis (x in this case). Repeat the same calculation with all of the same parameters, except change the spectral window to 500-1000 nm in 10 steps. Save the scattering, absorbance and extinction spectra. Look at the E-field cut plane visualization to see what the field distribution looks like. Which axis is the field localized to? Next repeat the calculation with the same shape, but (on the first tab) change the target rotation to 90° in x. Rerun the calculation. Save the scattering, absorbance and extinction spectra. Now which axis have we excited? How do the spectra of the long and short axis differ in terms of their resonance peak? Which one has higher extinction? Now change SHPAR 3 to make the aspect ratio larger. How do the long-axis and short-axis peaks differ depending on aspect ratio of the rod? Discuss these observations. (see *J. Phys. Chem. B*, **2001**, *105* (19), pp 4065–4067).

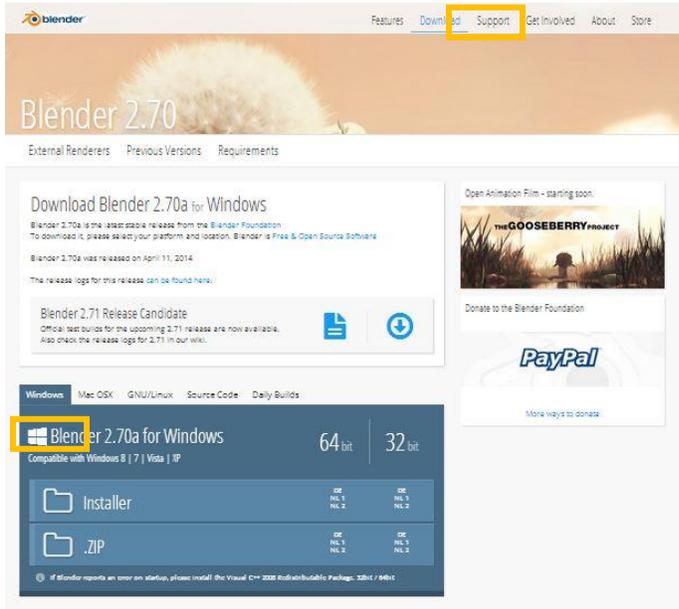
Dielectric Sensing

In the first tab of the DDA tool, reset the shape to “concentric ellipsoids”. This will generate an ellipsoid of one dielectric material with a shell of another dielectric material. Set the SHPAR 4, 5, and 6 = 70 nm and set the dielectric of this material to SiO_2 to make a silica nanoparticle core 70 nm in diameter. Next, set the SHPAR 1, 2, and 3 to either 74, 80, or 90 nm to make a symmetric shell around the silica nanoparticle of 4, 10, or 20 nm. Set the dielectric of this material to Au. For the spectrum, choose 500 to 700 nm, in 10 divisions. Set the refractive index of the medium to $n=1$. Run the simulation, save, and plot the extinction spectra. Now change the refractive index of the medium to $n=1.2$ and run the simulation again. Increase the refractive index of the medium another time to $n=1.4$ and the run the simulation again. Plot the peak maximum of the extinction as a function of medium refractive index. Now compare with another person or group who used a different shell thickness. How does the sensitivity of the peak maximum with respect to medium refractive index change based on the thickness of the gold shell? (See *J. Phys. Chem. C*, **2007**, *111*, (47), 17451-17454.)

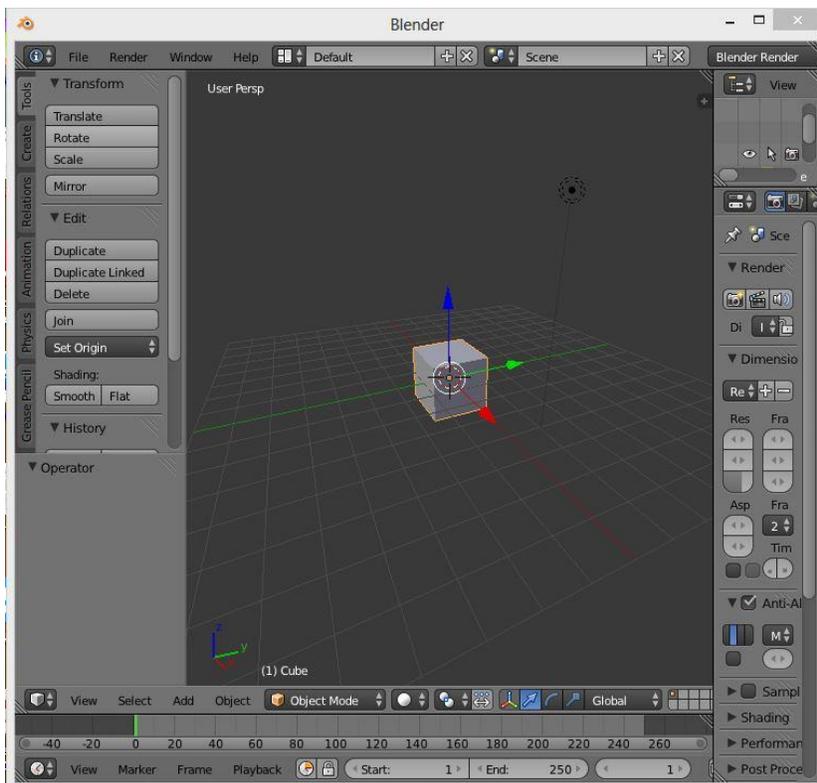
Homework

Simulations of New Geometries of Metal Nanoparticles

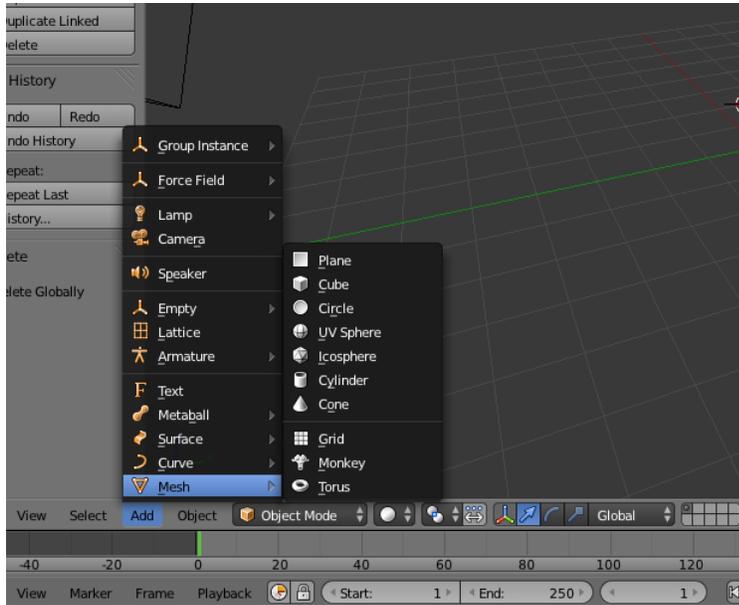
The DDSCAT tool has a collection of fixed geometries such as ellipsoids and cylinders that can be used to generate shape files but arbitrary geometries of interest can be provided by the user. These geometries can be created in common design applications such as “Blender”, CAD or any software which can generate a triangular mesh .obj file. Download and setup Blender from the site www.Blender.org. Select your system from the menu and download and run the program.



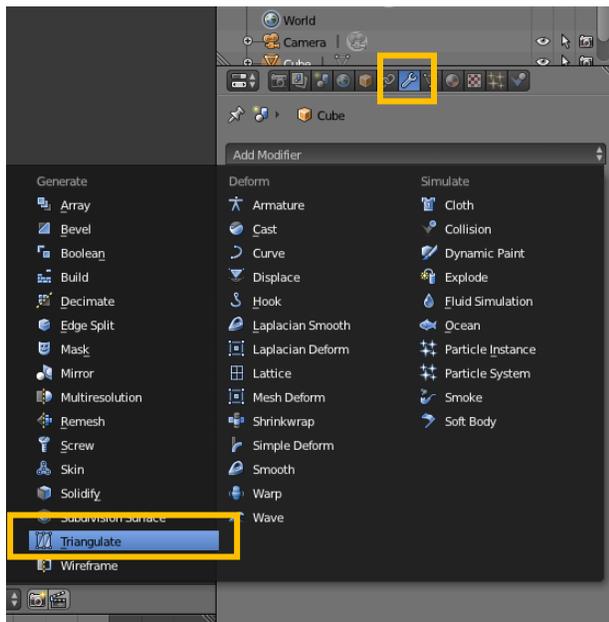
When you open Blender you will see a screen light this:



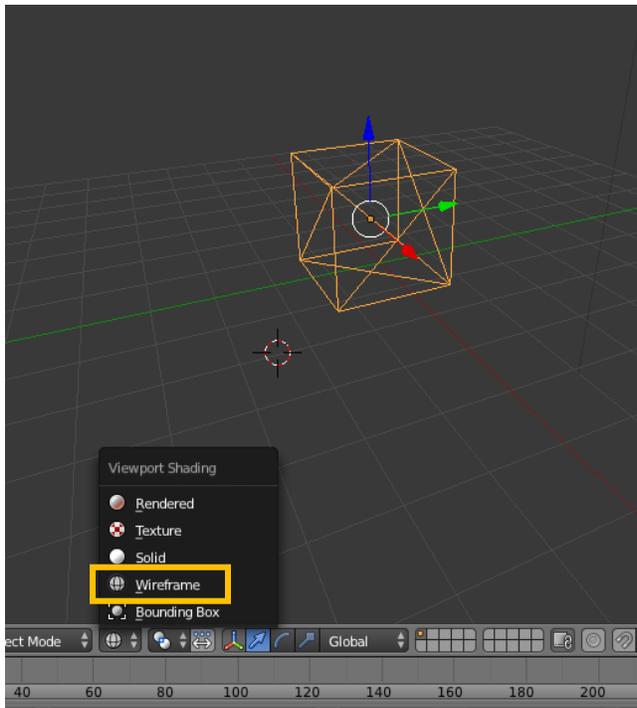
You start with a default cube as an object, or mesh, in the center of the screen. Blender is capable of making meshes into an arbitrary shape, but for this demo we will simply export one of the preset shapes. Delete the cube by hitting “delete” on the keyboard. Then on the menu at the bottom of the screen, selected “Add”, then “Mesh” and select a shape to add. Note: Note that whatever shape you create, it is crucial that the geometric model must be a closed object – so a sheet would not work but a rectangular prism will. Make sure the object is selected. You can do this by right clicking on the object.



Now, on the right-hand side of the screen, there will be a menu of icons. Select the icon that looks like a wrench to add a modifier to the object. Click the “Add Modifier” menu and select “Triangulate” and then “Apply”. This creates a triangulated mesh.



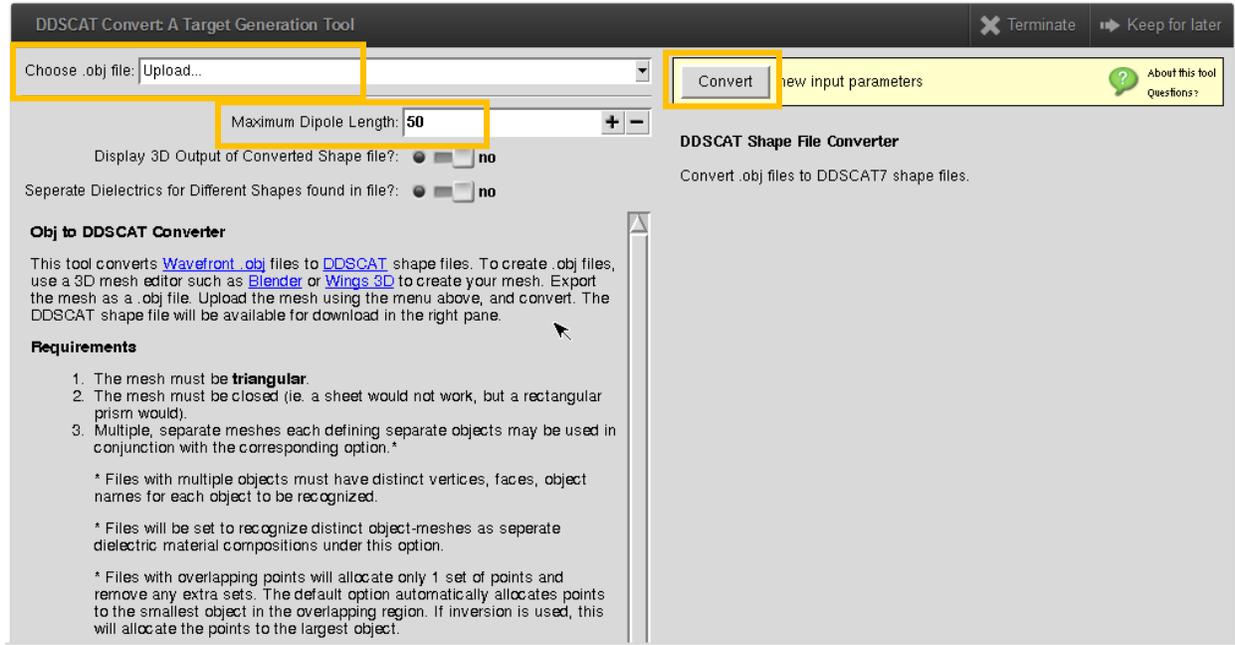
To make sure this worked, on the bottom menu there is an icon that should look like a solid sphere. Click on this menu and change from “Solid” to “Wireframe”. You should be able to see that the shape consists of triangular sections now.



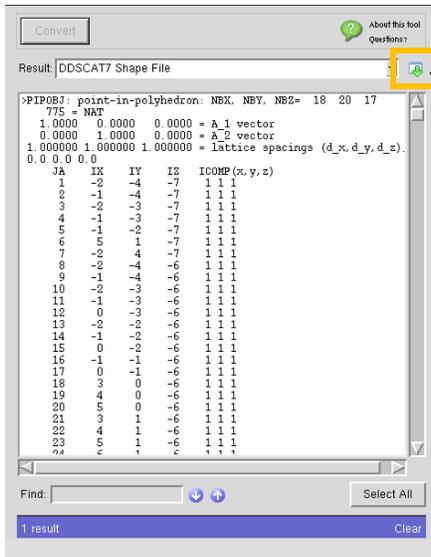
Finally, go to the “File” menu and select “Export” and then “Wavefront (.obj)”. Select a location to save the OBJ file.

Before these files can be input into DDSCAT, however, they must be transformed into a collection of dipoles – which is the role of the nanoHUB tool, DDA Conversion Tool.

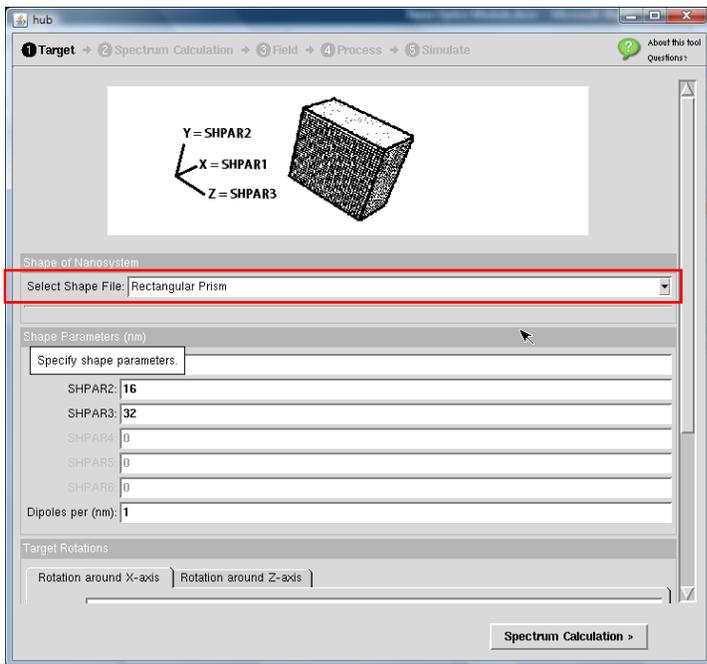
Launch the tool from the nanoHUB website. Select “Upload” from the “Choose .obj file” box. This will prompt a pop-up window in which you select the OBJ file generated in Blender. Next select the “Maximum dipole length” or the number of dipoles that spans the largest dimension of the uploaded shape.



Now hit “Convert”. The shape file will appear in the right hand side of the screen. Download the shape file by hitting the download button on the upper right. Save the file.



This file can now be uploaded to the DDSCAT tool used in the previous exercises in place of the one of the target shaped provided by the tool. Under the select shape file box, choose upload custom shape from file. This will allow you to input the shape you generated.



Select 1 dipole per nm as the resolution (this will generally work unless you generate a shape with many sharp corners).

On the second tab set the wavelength range to something fairly large (400-1000 in perhaps 30 steps should work).

On the third tab select E^2 for the near field calculation.

On the fourth tab select remote parallel DDSCAT with wavelength splitting. This will run the calculation on a remote cluster, and will allow for much fast convergence with the arbitrary geometry.

By default the calculation results will be visible on nanohub.org for one week if you simply close your browser and do not terminate your session. This will allow you to share your generate spectra and field distribution with the class the following week. Some observations you may want to make are:

What does the spectra look like?

Is my object primarily scattering or absorbing light?

Where are the positions of high field located and how does this correspond with the geometry of the shape?