

# Documentation for SWXF demo file

Laurence Lurio

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## 1 Introduction

The file `SWXF_example_nov_2021.py` is an example file modeling the approach for calculating the expected signal from an x-ray standing wave fluorescence experiment. Sections in the code are marked off by `"###"`. Below we go through the sections one at a time

## 2 Section 1

In this section physical and mathematical constants are imported from `scipy.constants`. To the extent possible MKS units are assumed through the code. However, this is not always possible, as, for example, some of the functions in the x-ray database require energies in eV units. I will try to make the conversions obvious when they occur. Otherwise assume MKS. Metric prefixes are then used to convert from MKS. For example, `44*centi` will be used to represent centimeters, where the unit of "meters" will have to be inferred from context. It is possible to attach units to quantities in python using the `pint` package, but this leads to complications when you use arrays, so I am skipping it.

## 3 Section 2

Here we define the fluorescent tag as a 5 nm diameter gold nanoparticle. I'm not sure if that will be the actual size of the nanoparticle used for fluorescent tags, this is something we need to consult on with Dr. Gaillard and the literature. But given the nanoparticle diameter, and assuming it is spherical, we can then calculate the number of atoms which we will need to get the fluorescent cross section.

## 4 Section 3

In section 3 we define the surface coverage in terms of the distance between gold nanoparticles on the surface. If we put one gold label per protein then this is the distance between proteins on the surface. We need to consult the

literature to see what is a reasonable packing density of proteins in a supported lipid film. I guessed a spacing of every 100 nm. Perhaps this is conservative, we can probably pack them denser, but at some point they begin to interact with each other. However the denser the protein packing the stronger the signal.

## 5 Section 4

In section 4, we calculate the atomic absorption cross section. The atomic absorption cross section is given by the imaginary part of the atomic scattering factor  $f_2$  via

$$\sigma = 2f_2r_0\lambda. \quad (1)$$

We then correct this by the fluorescent yield in order to only calculate the fraction of absorbed x-rays that result in fluorescence.

Given a cross section per atom  $\sigma_a$  we would like to calculate the total scattering cross section  $\sigma_T$ . This will depend on the number of atoms intercepted by the beam. The total number of fluorescent photons produced is given by

$$N = \Phi\sigma_T \quad (2)$$

Here  $\Phi$  is the incident beam flux (photons/m<sup>2</sup>). However, typically we specify the beam in terms of the beam intensity  $I_0$  and the area of the beam  $A_0$ . In this case  $\Phi = I_0/A_0$ . Assume that we have a density of atomic scatterers  $\rho_N$  each with cross section  $\sigma$ . Then the total cross section of scatterers in the beam is  $\sigma_T = \rho_N\sigma_a A_0\Lambda$ . Here  $\Lambda$  is the thickness of the sample. Thus we can rewrite eq. 2 as:

$$N = \frac{I_0}{A_0}\rho_N\sigma_a V = \frac{I_0}{A_0}\rho_N\sigma_a A_0\Lambda = I_0\rho_N\sigma_a\Lambda \quad (3)$$

We actually have a surface density of scatterers  $S_N$  not a volume density,  $\rho_N$ . To convert between surface density and volume density we can use  $\rho_N = S_N/h$  where  $h$  is the height of the beam.

We can now calculate the total fluorescence yield given the beam intensity,  $I_0$ . Let  $h$  be the beam height and  $\alpha$  the incident angle. Since the beam comes in at grazing incidence, the thickness of sample intercepted by the beam is  $\Lambda = h/\alpha$ . Putting this into eq. 3 gives:

$$N = I_0 \frac{S_N}{h} \sigma_a \Lambda = I_0 \frac{S_N}{h} \sigma_a \frac{h}{\alpha} = I_0 S_N \sigma_a / \alpha \quad (4)$$

## 6 Reflectivity functions

Here we discuss the functions `n_elem(elem,E)`, `n_water(E)`, `swave(alpha,z,E)` used to calculate the standing wave. The function `n_elem(elem,E)` takes an element and finds the x-ray index of refraction at the energy  $E$  given in eV. The function `n_water(E)` calculates the index of refraction for water. Since we are assuming scattering from a phospholipid bilayer submerged in water, these two materials form the interface if we ignore the bilayer.

The function `swave(alpha,z,E)` calculates the reflectivity of the interface from Fresnel's laws using the indices of refraction, then sums the incident and reflected waves and squares them to find the intensity of the standing wave at height  $z$  relative to the surface. We approximate Fresnel's laws in the limit of small angles. Here we can ignore polarization and we get

$$R(\alpha) = |r(\alpha)|^2 = \left| \frac{\alpha - \alpha'}{\alpha + \alpha'} \right|^2 \quad (5)$$

Here  $\alpha$  is the incident angle and  $\alpha' = \sqrt{\alpha^2 - \theta_c^2}$  and  $\theta_c$  is the critical angle for total external reflection.

The critical angle is given by Snell's law. This is typically written as

$$\frac{\sin(\phi_1)}{\sin(\phi_2)} = \frac{n_2}{n_1} \quad (6)$$

Where the angles  $\phi_1$  and  $\phi_2$  are defined with respect to the surface normal. Since in x-ray scattering the angles are typically defined with respect to the surface rather than the surface normal, we can write  $\theta = 90 - \phi$  and thus  $\sin(\phi) = \sin(90 - \theta) = \cos(\theta)$ . Thus the condition for the critical angle is that  $\cos(\theta_2) = 1$  since for smaller angles  $\cos(\theta_2)$  would have to exceed 1, which implies an imaginary angle. Thus we can write the expression for the critical angle as:

$$\theta_c = \arccos\left(\frac{n_2}{n_1}\right) \quad (7)$$

We can also calculate the transmission of the interface

$$T(\alpha) = |t(\alpha)|^2 = \left| \frac{2\alpha}{\alpha + \alpha'} \right|^2 \quad (8)$$

Given Snell's law and the reflection and transmission coefficients we can then calculate the x-ray field intensity above and below the interface. Below the interface the electric field is given by  $E_T = tE_0 e^{i\vec{k} \cdot \vec{r}} = tE_0 e^{ik_0 z \sin(\alpha')}$ . Here  $z$  is the height above (or below) the surface. This gives for the transmitted intensity,  $I_T$ :

$$I_T = I_0 T e^{ik_0 z (\sin(\alpha') - \sin(\alpha')^*)} \quad (9)$$

Normally, the exponential term cancels out, however, below the critical angle the refracted angle is purely imaginary so that this term leads to an exponential decay with  $z$ .

Above the surface we have the sum of two waves

$$E = E_0 \left( e^{ik_0 z \sin(\alpha)} + r e^{-ik_0 z \sin(\alpha)} \right) \quad (10)$$

giving the intensity  $I = |E|^2$  which oscillates as a cosine

$$I/I_0 = 1 + r^2 + r \left( e^{2ik_0 z \sin(\alpha)} + e^{-2ik_0 z \sin(\alpha)} \right) = 1 + r^2 + 2r \cos(2k_0 z \sin(\alpha)) \quad (11)$$

Note that this results in a standing wave with an oscillation period of These relations are used in `swave(alpha,z,E)` to find the intensity of standing wave above and below the interface.

Note that we don't really need the intensity of the standing wave below the interface in order to calculate the fluorescence since the gold is above the interface, but we might need this later to estimate background scattering from the surface.

Also, note that this scheme is only an approximation. The reflection from the interface will be modified by the presence of the bilayer. However we will deal with that correction later.

For now there are two separate versions of the function `swave(alpha,z,E)`. `swave_z(alpha,z,E)` allows you to submit an array of incident z-values for a fixed angle and `swave_a(alpha,z,E)` allows you to submit an array of incident angles for a fixed height.

## 7 Section 6 from demo code

In section 6, the functions are used to create plots. The first graph looks at the standing wave intensity vs. height for a fixed incident angle. This gives an indication of how sensitive the technique is to the position of the nanoparticle. The second graph plots the fluorescence yield vs. angle for a nanoparticle at a fixed height.

## 8 Compton Scattering Background

A large source of background signal in the SWXF experiment results from Compton scattering. [1]. Here we go through an analysis of the main source of Compton scattering from the water filling the experimental cell and compare it with the expected fluorescence signal from the gold nanoparticles.

The intensity of Compton scattering is given in eq. 1.16 in Warren [1]. Note that he calls this "modified" rather than Compton scattering, but that is just a terminology issue. In addition since we are using synchrotron radiation, which is polarized, we cannot take the approximation of unpolarized radiation which Warren uses. Thus we replace his term  $\frac{1+\cos^2(2\theta)}{2}$  with  $\sin^2(\alpha)$  where the angle  $\alpha$  is the angle between the scattered radiation direction and the polarization direction of the x-rays. Further, if we rewrite eq. 1.16 from Warren in terms of the detector solid angle and the number of counts per second in the detector,  $N_C$  and  $I_0$  the flux of the incident beam (photons/m<sup>2</sup>/s) and if we use the notation  $r_0 = \frac{e^2}{mc^2}$  (or in MKS units  $r_0 = \frac{e^2}{4\pi\epsilon_0 mc^2}$ ) we obtain;

$$N_C = I_0 r_0^2 \sin^2(\alpha) i(M) d\Omega \quad (12)$$

Here:

$$i(M) = Z - \sum_{n=1}^Z f_{en}^2 \quad (13)$$

Warren gives an example of how to calculate  $f_e$ , and thus  $i(M)$ . However these quantities are most easily (and more accurately) looked up in a database which is given in the example python code. Note also, that the discussion in Warren concerns calculating x-ray scattering factors for neutral atoms. For molecules, the scattering factors are more complicated because some electrons are in molecular orbitals. The easiest way to deal with this for the case of water is to assume water is H<sub>2</sub>O and treat the electrons as exclusively orbiting the oxygen atoms. Thus we treat each molecule of H<sub>2</sub>O as simply a doubly negative oxygen ion. An example of code that can calculate  $i(M)$  for a molecule of water is given in the example file `water_compton.py`.

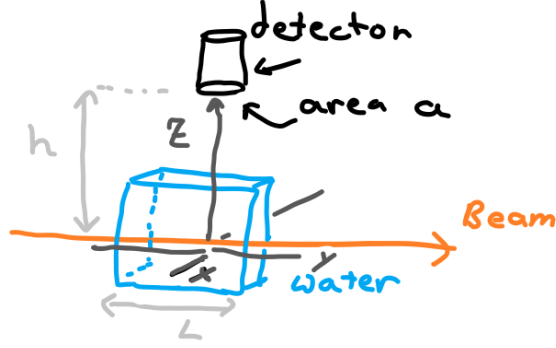


Figure 1: Geometry for water compton scattering calculation

For the simplest calculation, just assume the beam goes through the water on a straight line (see fig. 1). Assume a very narrow beam going through a length  $L$  of water. Suppose the beam goes from  $y = -L/2$  to  $L/2$ . Take the detector to be a small area  $a$  located at  $y = 0, z = h$  so that  $d\Omega = \frac{a}{y^2 + h^2}$ . Lets assume the polarization of the x-ray beam is perpendicular to the scattering plane, so the  $\sin(\alpha)$  term is 1. Then the Compton scattering background is given by

$$N_C = N_0 \int_{-L/2}^{L/2} \frac{r_e^2 i(M) \rho_w N_A a}{A_w (y^2 + h^2)} dy \quad (14)$$

Here  $A_w = 18.01528$  g/mol is the atomic weight of water.

We would like to compare this with the total fluorescence yield. To do this we need the atomic cross section for fluorescence. The atomic absorption cross section is given by

$$\sigma = 2\lambda r_0 f'' \quad (15)$$

Here  $f''$  is the imaginary part of the atomic scattering factor, which can be looked up in tables. The fluorescence is emitted uniformly over  $4\pi$  steradians, so that the photons scattered into a detector of solid angle  $d\Omega$  by an atom illuminated by an incident flux of  $I_0$  photons/m<sup>2</sup> is

$$N_f = I_0 2\lambda r_0 f'' \frac{d\Omega}{4\pi} \quad (16)$$

Comparing eq. 16 with eq.12 gives (per atom)

$$\frac{N_f}{N_C} = \frac{2\lambda f''}{4\pi r_0 \sin^2(\alpha) i(M)} \quad (17)$$

We will be interested in both the total magnitude of the Compton scattering entering the detector in order to see if we are saturating the detector and the ratio of the Compton to fluorescence in order to see if we can see the peak due to the fluorescence without being washed over by the tail of the peak from the Compton scattering.

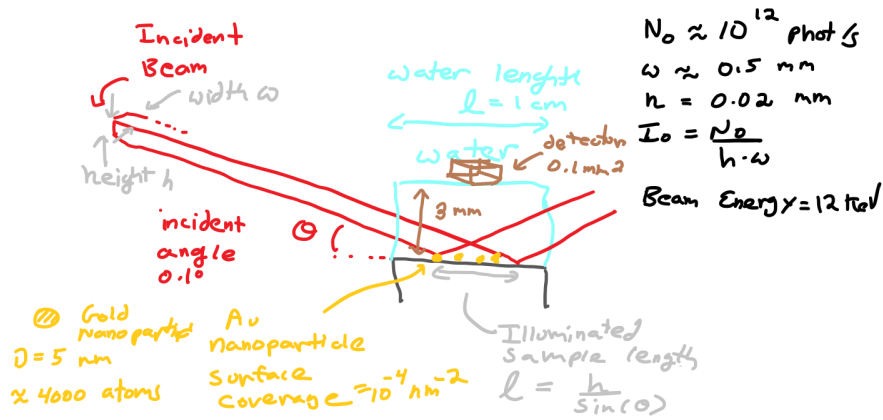


Figure 2: Some numbers for the calculations of fluorescence intensity

If this makes sense, here are some suggestions for how to proceed next. Some further details of the geometry and numbers are given in fig. 2

1. Calculate the total scattering from eq. 14 into a small detector (use  $100 \text{ micron} \times 100 \text{ micron}$ ) for a geometry similar to the experimental cell I sent you. Assume that the x-ray polarization is perpendicular to the scattering plane so that the  $\sin(\theta)$  term is 1.
2. Find the ratio of Compton to fluorescent scattering by using the gold coverage assumed in the SWXF\_example file. (Look at lines 33-48 of that file for more details. Note that for a reflected beam from a surface the Compton is increased by a factor of 2, but if the gold is at the peak of the standing wave the gold scattering is increased by a factor of 4, so you get an additional gain of 2.
3. Repeat this calculation for the polarization in the scattering plane. This is actually the preferred orientation, since at exactly 90 degrees the polarization is parallel to the scattering direction so that the Compton scattering is zero. However, when you integrate over  $dx$ , you will not get zero since the angle  $\phi$  changes as  $x$  increases.
4. Set up an integral over a large detector by using your small detector element as the argument for the integration.

## 9 Things to try next

1. Plot a graph of fluorescence yeild vs. particle size, or area coverage (trivial)
2. Superimpose plots of fluorescence yield vs. angle for different heights of nanoparticle
3. Calculate the fraction of fluorescence that would get into a detector for an acheivable experimental setup.
4. Modify the code to include the reflectivity from an interface with a bilayer.
5. Modify the code to include an estimate of Compton scattering background

## References

- [1] B E Warren. *X-Ray Diffraction*. Dover, Toronto, 1990.