Surface plasmon resonance (SPR) modeling & analysis

This workbook models the reflectance equations in the Simon, Mitchell & Watson paper, American Journal of Physics, Vol. 43, No. 7, pp. 630-636 (1975).

Use this template as a starting point to carry out the analysis tasks. For reference, here are links to recommended Python resources: the Whirlwind Tour of Python and the Python Data Science Handbook both by Jake VanderPlas.

Standard Packages

This is a good idea at the beginning of your notebook to include the packages that you will need. We will use those shown below here. A brief description:

- `numpy` is the foundational package for Python numerical work. It extends and speeds up array operations beyond standard Python, and it includes almost all math functions that you would need for example `sqrt()` (square root) or `cos()` (cosine). These would be written in code as `np.sqrt()` or `np.cos()`.
- `scipy` is a huge collection of scientific data analysis functions, routines, physicical constants, etc. This is the second most used package for scientific work. Here we will use the physical constants library, `scipy.constants`. Documentation is at SciPy.org with the constants subpackage at https://docs.scipy.org/doc/scipy/reference/constants.html.
- `uncertainties` is a very useful small package that simplifies uncertainty propagation and printing out of quantities with uncertainty. Documentation is at https://pythonhosted.org/uncertainties/
- `matplotlib` is *the* standard plotting package for scientific Python. We will use a subset called `pyplot` which is modeled after the plotting functions used in MATLAB. The last line below, `%matplotlib inline`, simply forces the plots to appear within the notebook.
- `pandas` is a large data science package. It's main feature is a set of methods to create and manipulate a "DataFrame," which is an enlargement of the idea of an array. I plays well with NumPy and other packages. We will use it mainly as a way to read files into data sets in an easy way.
- LMFit is excellent for carrying out line and curve fits with many useful features.

Getting Help

See the example code for a wide range of actions in notebooks created by Prof. Marjorie Olmstead and Prof. David Pengra in this repository: **Physics431/Examples**.

You can pull the examples into your environment with the following command. (Only do this once, or you will get an error):

```
git clone https://github.com/Physics431/Examples
```

Task Summary

The SPR modeling analysis program creates a curve following the reflectance formula given in the paper by Simon, Mitchell and Watson, Eq. (11). Your task is to recreate this function with Python code and plot it under your data points for at least one or two data sets. This will give you deeper insight into the fitting formula.

Start by creating functions for the quantities that go into Eq. (11). These are Eqs. (7), (9b) and (9c), along with Eqs. (10a) and (10b). The quantities that feed in are the complex dielectric permittivity and the index of reflection of the glass n, along with $\omega/c = k_0 = 2\pi/\lambda$.

Then combine the functions into a single one that gives the reflectance R, Eq. (11).

Be careful to convert your angles from degrees to radians before feeding them to the functions! (This is the most common mistake students make.)

You will need to make sure all quantities are represented by complex data types, even if the physical quantity is real-valued.

Once you have a working function, you may try to see if you can make it work with LMfit. In principal this is possible, but prepare for some challenges if your function is not of the required form for LMfit's library calls.

In [161…

```
# Usually import packages via a handle to the functions in them using import ... as
#
import numpy as np
import matplotlib.pyplot as plt
import matplotlib as mpl
import pandas as pd
import uncertainties as unc
import scipy.constants as const
import cmath as cm
import numpy.lib.scimath as SM
%matplotlib inline
```

In [3]:

```
# Useful plot default
mpl.rcParams['figure.figsize'] = 12.0,6.0  # Roughly 12 cm wde by 8 cm high
mpl.rcParams['font.size'] = 14.0 # Use 14 point font
```

Reflectance modeling equations

Main equation for normalized reflected intensity (SMW, Eq. 11):

$$R = \left| \frac{r_{pm} + r_{ma} \exp(-2kd)}{1 + r_{pm} r_{ma} \exp(-2kd)} \right|^2$$

where r_{pm} and r_{ma} are the reflection amplitudes from the prism-metal interface and the metal-air interface, and d is the film thickness.

The parameter k is the "absorption coefficient at non-normal incidence" (SMW, Eq. 7):

$$k = -i\frac{\omega}{c}\left(\epsilon - n^2 \sin^2\theta_1\right)^{1/2}$$

We replace ω/c with the wavenumber in free space $k_0 = 2\pi/\lambda_0$ of the incident light.

The reflection amplitudes are given by (SMW, Eq. 9b)

$$r_{pm} = \frac{\epsilon^{1/2}\cos\theta_1 - n\cos\theta_2}{\epsilon^{1/2}\cos\theta_1 + n\cos\theta_2}$$

and (SMW, Eq. 9c)

$$r_{ma} = \frac{\cos\theta_2 - \epsilon^{1/2}\cos\theta_3}{\cos\theta_2 + \epsilon^{1/2}\cos\theta_3}$$

where (SMW, Eq. 10a)

$$\cos\theta_2 = \left(1 - (n^2/\epsilon)\sin^2\theta_1\right)^{1/2}$$

and (SMW, Eq. 10b)

$$\cos\theta_3 = \left(1 - n^2\sin^2\theta_1\right)^{1/2}$$

Create functions for the above equations

Make Python functions that carry out the calculations for each of the above equations.

To evaulate the functions, you will need the following constants

- The values of the wavelengths for the green and red laser light in vacuum
- The values of the prism's refractive index for those two wavelenths

The arguments to the function will include

- The incident angle θ_1 in radians(!)
- The complex dielectric permittivity ϵ
- The metal film thickness d

The functions should all return complex values except the one for Eq. (11) the reflectance R. If you convert all inputs to the functions to complex, the return value will automatically be complex.

Units: if k is in inverse nanometers, then d should be in nanometers, otherwise all othe constants are unitless.

In [76]:
```
# Enter the appropriate values
wavelength_green = 543.5 #nanometers
wavelength_red = 632.8 #nanometers
N_red = 1.515 # unitless
N_green = 1.519 # unitless

d_default = 50 # nanometers
eps_default = -10
one = complex(1.0, 0.0)
minus_i = complex(0.0, -1.0)

wavenum_red = 2.0*np.pi/wavelength_red
wavenum_green = 2.0*np.pi/wavelength_green
```

Build the functions.

In [133…
```
# For each function fill in the details

def cos_theta2(theta_1, epsilon, N):
    # You code this
    cos_th2 = SM.sqrt(one - N**2 * np.sin(theta_1)**2/(epsilon))

    return cos_th2

def cos_theta3(theta_1, N):
    # You code this
    cos_th3 = SM.sqrt(one - N**2 * np.sin(theta_1)**2)

    return cos_th3

def k_plas(theta_1, epsilon, N, wavenum):
    # You code this
    k_p = minus_i*wavenum*SM.sqrt(epsilon-N**2*np.sin(theta_1)**2)

    return k_p

def r_ma(theta_1, epsilon, N):
    # You code this
    r_23 = (cos_theta2(theta_1,epsilon,N)-SM.sqrt(epsilon)*cos_theta3(theta_1,N))/(

    return r_23

def r_pm(theta_1, epsilon, N):
    # You code this
    r_12 = ((SM.sqrt(epsilon)*np.cos(theta_1))-(N*cos_theta2(theta_1,epsilon,N)))/(

    return r_12

def R(theta_1, epsilon = eps_default, d=d_default, N = N_red, wavenum = wavenum_red
    # You code this
    big_R = (r_pm(theta_1,epsilon,N)+r_ma(theta_1,epsilon,N)*np.exp(-2*k_plas(theta
    big_R = np.abs(big_R)**2

    return big_R
```

Test the reflectance

Test the above functions by feeding in a range of angles typical for the experiment, say between 41 and 50 degrees. (Don't forget to convert to radians, or you will get some strange looking curves.) Use your fit resuslts from the LabVIEW analysis.

You can use the NumPy function `np.linspace()` to genrate an array of evenly spaced values between a lower and upper limit. For example to get an array of 500 numbers between 41 and 50, do this:

```
angles =  np.linspace(41.0,50.0,500)
```

In [143…

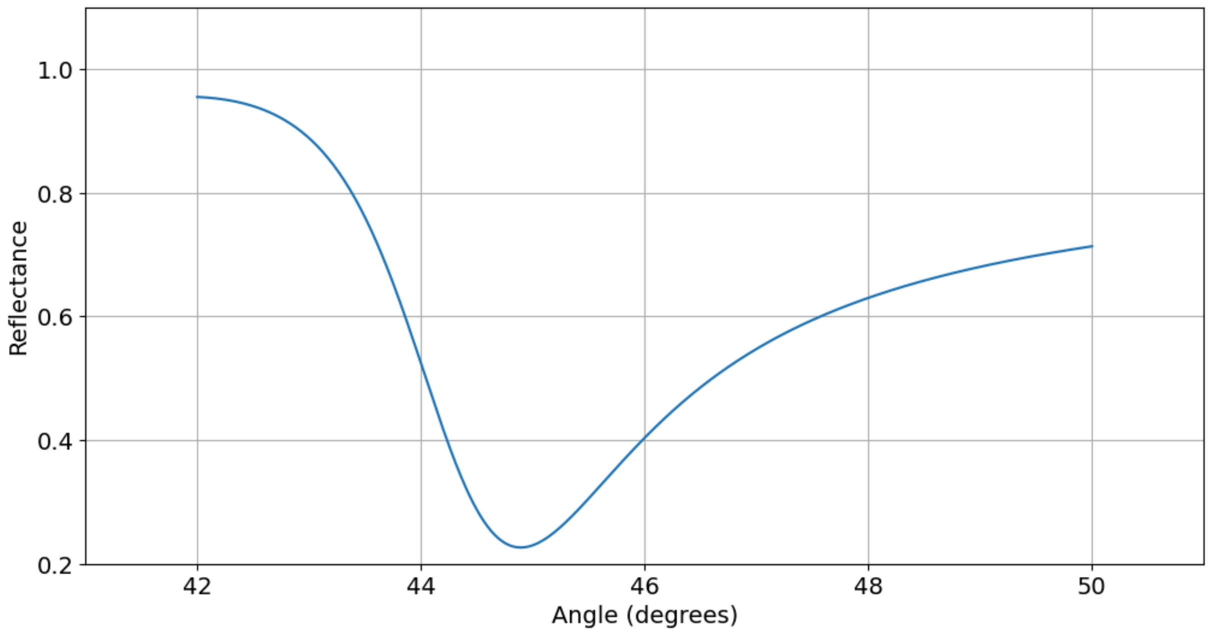
```
angles = np.linspace(41.0, 50.0, 500) # set a range of angles
rad_angles = (np.pi/180.0)*angles # convert them to radians to pass to your functio

my_eps = complex(-9.03, 0.828) # enter a value of epsilon
my_d = 40.369 # enter a value of thickness
```

Make a plot

Make a quick plot to test it.

In [154…

```
# Pass the above variables to your functions and plot them
#
# See the examples for how to make a plot

reflections = R(theta_1 = rad_angles, epsilon = my_eps, d = my_d)

plt.plot(angles, reflections)
plt.xlabel('Angle (degrees)')
plt.ylabel('Reflectance')
plt.ylim(0.2, 1.1)
plt.xlim(41, 51)
plt.grid(True)
```



Plot the model against data

Read in a data file

The data files are simple tab-delimited text files that can be read in with Pandas `pd.read_csv()`:

```
red3_data = pd.read_csv('red_Ag_3.csv',sep='\t')
```

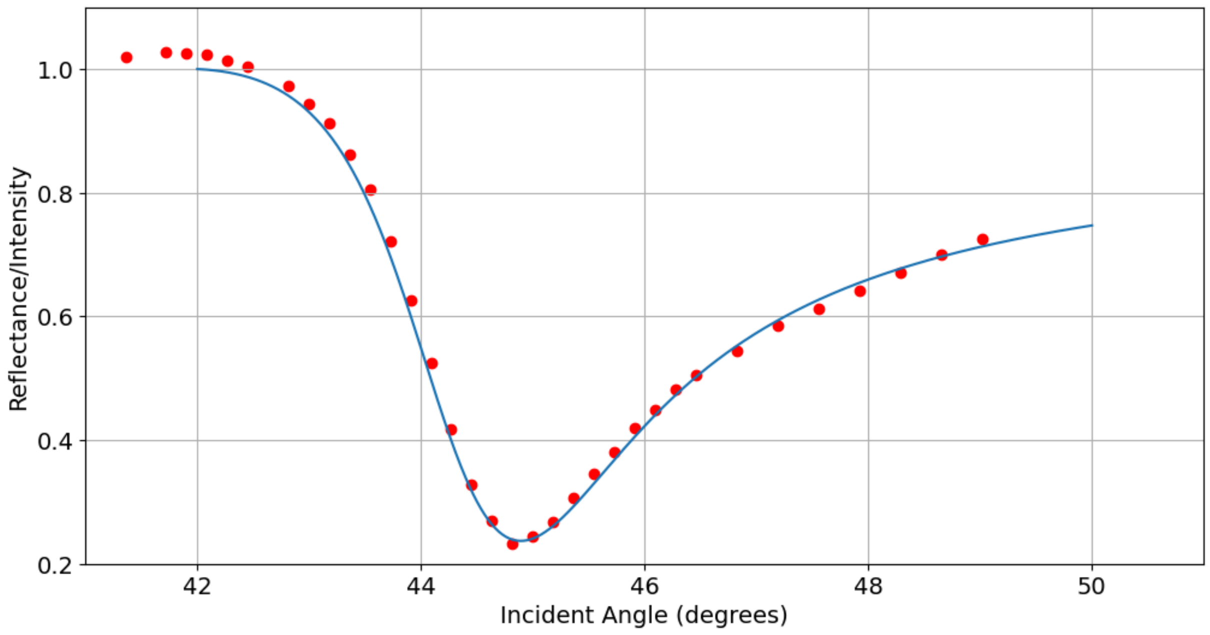
In [145…

```
# Read in  adata file and print it to see that it looks right
red2_data = pd.read_csv('RedP2', sep='\t')
print(red2_data)
```

```
    Theta (deg)  Intensity  Phi_A (deg)  Micrometer (mm)
0       41.3581     1.0201       5.5207            13.50
1       41.7222     1.0269       4.9679            13.00
2       41.9042     1.0260       4.6916            12.75
3       42.0863     1.0234       4.4154            12.50
4       42.2683     1.0145       4.1392            12.25
5       42.4504     1.0031       3.8631            12.00
6       42.8145     0.9735       3.3111            11.50
7       42.9966     0.9436       3.0351            11.25
8       43.1786     0.9129       2.7592            11.00
9       43.3607     0.8621       2.4832            10.75
10      43.5428     0.8044       2.2073            10.50
11      43.7249     0.7216       1.9315            10.25
12      43.9070     0.6253       1.6556            10.00
13      44.0891     0.5253       1.3797             9.75
14      44.2712     0.4180       1.1038             9.50
15      44.4534     0.3289       0.8279             9.25
16      44.6356     0.2699       0.5520             9.00
17      44.8178     0.2330       0.2760             8.75
18      45.0000     0.2451       0.0000             8.50
19      45.1823     0.2667      -0.2760             8.25
20      45.3645     0.3057      -0.5521             8.00
21      45.5468     0.3460      -0.8282             7.75
22      45.7292     0.3805      -1.1044             7.50
23      45.9116     0.4199      -1.3807             7.25
24      46.0940     0.4491      -1.6570             7.00
25      46.2764     0.4817      -1.9334             6.75
26      46.4589     0.5050      -2.2099             6.50
27      46.8240     0.5449      -2.7632             6.00
28      47.1893     0.5849      -3.3169             5.50
29      47.5548     0.6121      -3.8711             5.00
30      47.9205     0.6411      -4.4257             4.50
31      48.2864     0.6717      -4.9810             4.00
32      48.6526     0.7005      -5.5369             3.50
33      49.0190     0.7256      -6.0935             3.00
```

In [157…

```python
# Redo your plot above, but add the data to compare
#
plt.scatter(red2_data["Theta (deg)"], red2_data["Intensity"], color = 'red')
reflections_norm = 1/max(reflections)
plt.plot(angles,reflections*reflections_norm)
plt.xlabel('Incident Angle (degrees)')
plt.ylabel('Reflectance/Intensity')
plt.ylim(0.2, 1.1)
plt.xlim(41, 51)
plt.grid(True)
```



Try a fit with LMFit

Read the documentation on LMFit (see the links at the top) and/or study the examples in the **Examples** repository to see how to create a custom model function. Some hints:

- The independent variable is by default called `x`. Your fit function should also use this, and it needs to be the first argument passed to the function.
- You will want to separate the real and imaginary parts of epsilon into two separate (real) variables.
- Your fitting function does not have to have all of its arguments be fit parameters. If you assign some to fixed values, these can be left alone. You will need to declare which variable should be allowed to be adjusted by LMfit.
- The easiest way to accomplish all of the above is to make a "wrapper" function to pass to LMfit that simply calls your model function (after fixing the things above).

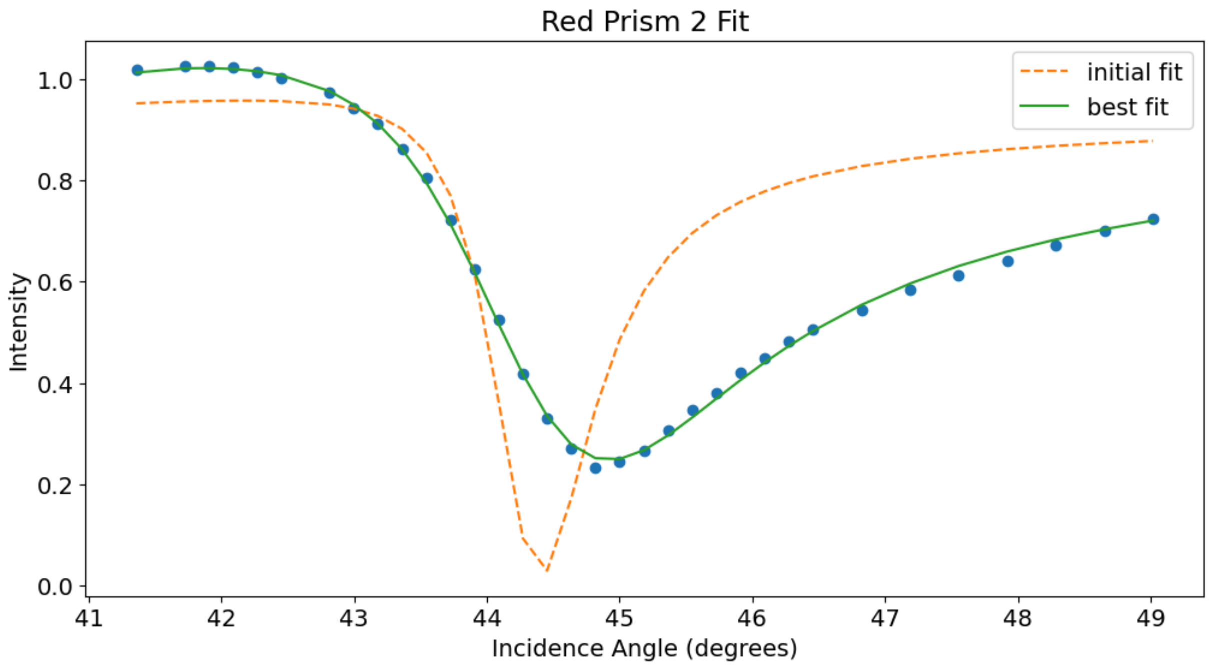
In [173…

```
# Create a fit function to build into a model

def R_fitter(x, eps_re, eps_im, d, I, N=N_red, wavenum=wavenum_red):
    return I*R(x*np.pi/180.0, epsilon=complex(eps_re,eps_im),
               d=d, N=N, wavenum=wavenum)

## Key statement to pull Model class in.
from lmfit import Model

## First argument is the function name.  The last argument is
#  passed directly to the fitting function and is not adjusted during thefit

model_red = Model(R_fitter, param_names=['eps_re','eps_im','d','I'],N=N_red, wavenu
model_green = Model(R_fitter, param_names=['eps_re','eps_im','d','I'],N=N_green, wa
```

In [170…
```
# Make and set the parameters to their starying values
# These should be close to what you got with the LabVIEW modeling program
red2_params = model_red.make_params(eps_re = -9.38, eps_im = 0.55, d = 58.70, I = 1
```

In [174…
```
# Run the fit
result_red2 = model_red.fit(red2_data['Intensity'],
                            red2_params, x=red2_data['Theta (deg)'])

# Print the results
print(result_red2.fit_report())

# Make a plot
theta_space_r2 = np.linspace(red2_data['Theta (deg)'].iloc[0],
                             red2_data['Theta (deg)'].iloc[-1], 500)
plt.plot(red2_data['Theta (deg)'], red2_data['Intensity'], 'o')
plt.plot(red2_data['Theta (deg)'], result_red2.init_fit, '--', label='initial fit')
plt.plot(red2_data['Theta (deg)'], result_red2.best_fit, '-', label='best fit')
plt.xlabel('Incidence Angle (degrees)')
plt.ylabel('Intensity')
plt.title('Red Prism 2 Fit')
plt.legend()

#Uncertainties of the fit
eps_re_red2_v = result_red2.params['eps_re'].value
eps_im_red2_v = result_red2.params['eps_im'].value
ep_re_r2_unc = result_red2.params['eps_re'].stderr
ep_im_r2_unc = result_red2.params['eps_im'].stderr

eps_re_red2 = unc.ufloat(eps_re_red2_v, ep_re_r2_unc)
eps_im_red2 = unc.ufloat(eps_im_red2_v, ep_im_r2_unc)
print(eps_re_red2, eps_im_red2)
```

```
[[Model]]
    Model(R_fitter, N='1.515', wavenum='0.009929180321080257')
[[Fit Statistics]]
    # fitting method   = leastsq
    # function evals   = 37
    # data points      = 34
    # variables        = 4
    chi-square         = 0.00277716
    reduced chi-square = 9.2572e-05
    Akaike info crit   = -312.031402
    Bayesian info crit = -305.925960
    R-squared          = 0.99884209
[[Variables]]
    eps_re: -8.99965633 +/- 0.02903288 (0.32%) (init = -9.38)
    eps_im:  0.83577262 +/- 0.00926135 (1.11%) (init = 0.55)
    d:       40.0220444 +/- 0.25464606 (0.64%) (init = 58.7)
    I:       1.07003927 +/- 0.00388800 (0.36%) (init = 1)
[[Correlations]] (unreported correlations are < 0.100)
    C(eps_re, d)      = +0.7845
    C(eps_im, I)      = +0.7350
    C(eps_im, d)      = -0.7320
    C(eps_re, eps_im) = -0.6629
    C(d, I)           = -0.4553
    C(eps_re, I)      = -0.3719
-9.000+/-0.029 0.836+/-0.009
```


Red Prism 2 Fit
initial fit
best fit
Intensity
Incidence Angle (degrees)