pycse - Python Computations in Science and Engineering

John Kitchin

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Contents

1 Overview

This is a collection of examples of using python in the kinds of scientific and engineering computations I have used in classes and research. They are organized by topics.

2 Basic python usage

2.1 Some basic data structures in python

Matlab post

We often have a need to organize data into structures when solving problems.

2.1.1 the list

A list in python is data separated by commas in square brackets. Here, we might store the following data in a variable to describe the Antoine coefficients for benzene and the range they are relevant for [Tmin Tmax]. Lists are flexible, you can put anything in them, including other lists. We access the elements of the list by indexing:

```
1 c = ['benzene', 6.9056, 1211.0, 220.79, [-16, 104]]
2 print c[0]
3 print c[-1]
4
5 a,b = c[0:2]
```

```
print a,b

name, A, B, C, Trange = c
print Trange
```

```
benzene
[-16, 104]
benzene 6.9056
[-16, 104]
```

Lists are "mutable", which means you can change their values.

```
a = [3, 4, 5, [7, 8], 'cat']
print a[0], a[-1]
a[-1] = 'dog'
print a
```

```
3 cat
>>> [3, 4, 5, [7, 8], 'dog']
```

2.1.2 tuples

Tuples are *immutable*; you cannot change their values. This is handy in cases where it is an error to change the value. A tuple is like a list but it is enclosed in parentheses.

```
a = (3, 4, 5, [7, 8], 'cat')
print a[0], a[-1]
a[-1] = 'dog'
```

```
3 cat
Traceback (most recent call last):
  File "<stdin>", line 1, in <module>
TypeError: 'tuple' object does not support item assignment
```

2.1.3 struct

Python does not exactly have the same thing as a struct in Matlab. You can achieve something like it by defining an empty class and then defining attributes of the class. You can check if an object has a particular attribute using hasattr.

```
class Antoine:
    pass

a = Antoine()
a.name = 'benzene'
a.Trange = [-16, 104]

print a.name
print hasattr(a, 'Trange')
print hasattr(a, 'A')
```

```
benzene
True
False
```

2.1.4 dictionaries

The analog of the containers.Map in Matlab is the dictionary in python. Dictionaries are enclosed in curly brackets, and are composed of key:value pairs.

```
s = {'name':'benzene',
     'A':6.9056,
     'B':1211.0}

s['C'] = 220.79
s['Trange'] = [-16, 104]

print s
print s['Trange']
```

```
{'A': 6.9056, 'C': 220.79, 'B': 1211.0, 'name': 'benzene', 'Trange': [-16, 104]}
[-16, 104]
```

```
s = {'name':'benzene',
     'A':6.9056,
     'B':1211.0}

print 'C' in s
# default value for keys not in the dictionary
print s.get('C', None)

print s.keys()
print s.values()
```

```
False
None
['A', 'B', 'name']
[6.9056, 1211.0, 'benzene']
```

2.1.5 Summary

We have examined four data structures in python. Note that none of these types are arrays/vectors with defined mathematical operations. For those, you need to consider numpy.array.

2.2 Basic math

Python is a basic calculator out of the box. Here we consider the most basic mathematical operations: addition, subtraction, multiplication, division and exponenetiation. we use the `print` to get the output. For now we consider integers and float numbers. An integer is a plain number like 0, 10 or -2345. A float number has a decimal in it. The following are all floats: 1.0, -9., and 3.56. Note the trailing zero is not required, although it is good style.

```
print 2 + 4
print 8.1 - 5
```

```
6
3.1
```

Multiplication is equally straightforward.

```
print 5 * 4
print 3.1*2
```

```
20
6.2
```

Division is almost as straightforward, but we have to remember that integer division is not the same as float division. Let us consider float division first.

```
print 4.0 / 2.0
print 1.0/3.1
```

```
2.0
0.322580645161
```

Now, consider the integer versions:

```
print 4 / 2
print 1/3
```

```
2
0
```

The first result is probably what you expected, but the second may come as a surprise. In integer division the remainder is discarded, and the result is an integer.

Exponentiation is also a basic math operation that python supports directly.

```
print 3.**2
print 3**2
print 2**0.5
```

```
9.0
9
1.41421356237
```

Other types of mathematical operations require us to import functionality from python libraries. We consider those in the next section.

2.3 Advanced mathematical operators

The primary library we will consider is `numpy`, which provides many mathematical functions, statistics as well as support for linear algebra. For a complete listing of the functions available, see http://docs.scipy.org/doc/numpy/reference/routines.math.html. We begin with the simplest functions.

```
1 import numpy as np
2 print np.sqrt(2)
```

```
1.41421356237
```

2.3.1 Exponential and logarithmic functions

Here is the exponential function.

```
1 import numpy as np
2 print np.exp(1)
```

```
2.71828182846
```

There are two logarithmic functions commonly used, the natural log function `numpy.log` and the base10 logarithm `numpy.log10`.

```
1 import numpy as np
2 print np.log(10)
3 print np.log10(10)  # base10
```

```
2.30258509299
1.0
```

There are many other intrinsic functions available in `numpy` which we will eventually cover. First, we need to consider how to create our own functions.

2.4 Creating your own functions

We can combine operations to evaluate complex equations. Consider the value of the equation $x^3 - \log(x)$ for the value $x = 4.1$.

```
1 import numpy as np
2 x = 3
3 print x**3 - np.log(x)
```

```
25.9013877113
```

It would be tedious to type this out each time. Next, we learn how to express this equation as a new function, which we can call with different values.

```
import numpy as np
def f(x):
    return x**3 - np.log(x)

print f(3)
print f(5.1)
```

```
25.9013877113
131.02175946
```

It may not seem like we did much there, but this is the foundation for solving equations in the future. Before we get to solving equations, we have a few more details to consider. Next, we consider evaluating functions on arrays of values.

2.5 Defining functions in python

Compare what's here to the Matlab implementation.

We often need to make functions in our codes to do things.

```
def f(x):
    "return the inverse square of x"
    return 1.0 / x**2

print f(3)
print f([4,5])
```

```
... ... >>> 0.111111111111
Traceback (most recent call last):
  File "<stdin>", line 1, in <module>
  File "<stdin>", line 3, in f
TypeError: unsupported operand type(s) for ** or pow(): 'list' and 'int'
```

Note that functions are not automatically vectorized. That is why we see the error above. There are a few ways to achieve that. One is to "cast" the input variables to objects that support vectorized operations, such as numpy.array objects.

```
import numpy as np

def f(x):
    "return the inverse square of x"
    x = np.array(x)
    return 1.0 / x**2

print f(3)
print f([4,5])
```

```
>>> ... ... ... ... >>> 0.111111111111
[ 0.0625  0.04  ]
```

It is possible to have more than one variable.

```
import numpy as np

def func(x, y):
    "return product of x and y"
    return x * y

print func(2, 3)
print func(np.array([2, 3]), np.array([3, 4]))
```

```
6
[ 6 12]
```

You can define "lambda" functions, which are also known as inline or anonymous functions. The syntax is `lambda var:f(var)`. I think these are hard to read and discourage their use. Here is a typical usage where you have to define a simple function that is passed to another function, e.g. scipy.integrate.quad to perform an integral.

```
from scipy.integrate import quad
print quad(lambda x:x**3, 0 ,2)
```

```
(4.0, 4.440892098500626e-14)
```

It is possible to nest functions inside of functions like this.

```
def wrapper(x):
    a = 4
    def func(x, a):
        return a * x

    return func(x, a)

print wrapper(4)
```

```
16
```

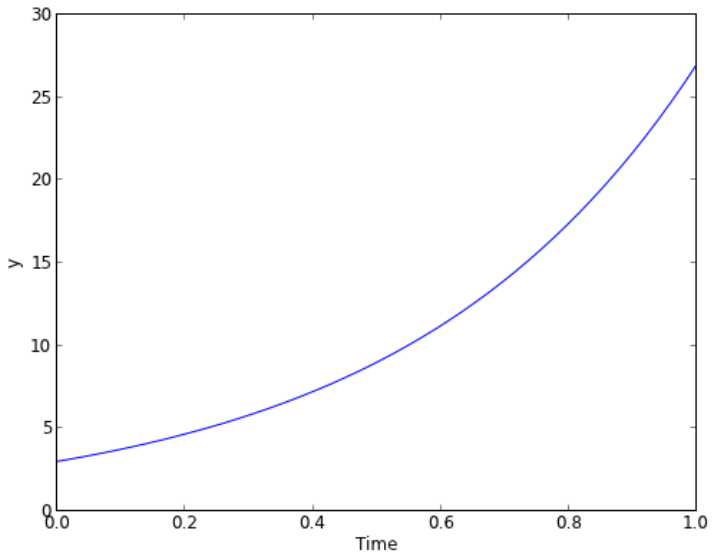
An alternative approach is to "wrap" a function, say to fix a parameter. You might do this so you can integrate the wrapped function, which depends on only a single variable, whereas the original function depends on two variables.

```
def func(x, a):
        return a * x

def wrapper(x):
    a = 4
    return func(x, a)

print wrapper(4)
```

```
16
```

Last example, defining a function for an ode

```
from scipy.integrate import odeint
import numpy as np
import matplotlib.pyplot as plt

k = 2.2
def myode(t,y):
    "ode defining exponential growth"
    return k * t

y0 = 3
tspan = np.linspace(0,1)
y =  odeint(myode, y0, tspan)

plt.plot(tspan, y)
plt.xlabel('Time')
plt.ylabel('y')
plt.savefig('images/funcs-ode.png')
```



2.6 Functions on arrays of values

It is common to evaluate a function for a range of values. Let us consider the value of the function $f(x) = \cos(x)$ over the range of $0 < x < \pi$. We cannot consider every value in that range, but we can consider say 10 points in the range. The `numpy.linspace` conveniently creates an array of values.

```
import numpy as np
print np.linspace(0, np.pi, 10)
```

```
[ 0.          0.34906585  0.6981317   1.04719755  1.3962634   1.74532925
```

```
2.0943951   2.44346095  2.7925268   3.14159265]
```

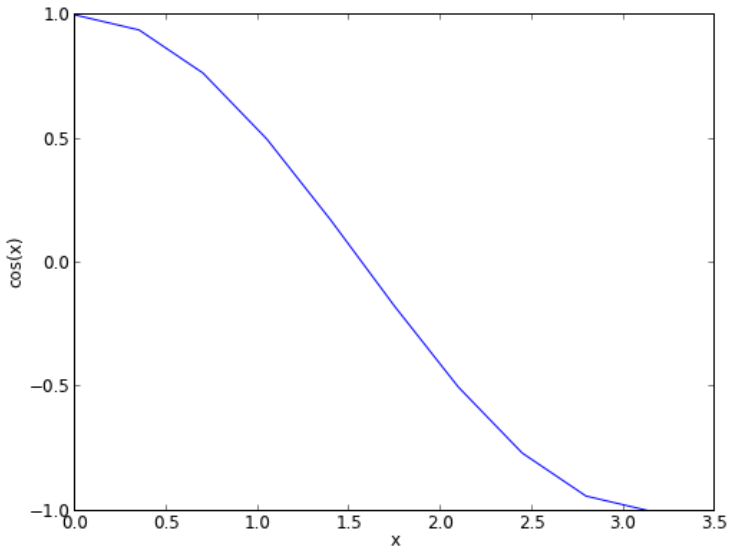
The main point of using the `numpy` functions is that they work element-wise on elements of an array. In this example, we compute the $\cos(x)$ for each element of x.

```
import numpy as np
x = np.linspace(0, np.pi, 10)
print np.cos(x)
```

```
[ 1.          0.93969262  0.76604444  0.5         0.17364818 -0.17364818
 -0.5        -0.76604444 -0.93969262 -1.        ]
```

You can already see from this output that there is a root to the equation $\cos(x) = 0$, because there is a change in sign in the output. This is not a very convenient way to view the results; a graph would be better. We use `matplotlib` to make figures. Here is an example.

```
import matplotlib.pyplot as plt
import numpy as np

x = np.linspace(0, np.pi, 10)
plt.plot(x, np.cos(x))
plt.xlabel('x')
plt.ylabel('cos(x)')
plt.savefig('images/plot-cos.png')
```



This figure illustrates graphically what the numbers above show. The function crosses zero at approximately $x = 1.5$. To get a more precise

value, we must actually solve the function numerically. We use the function `scipy.optimize.fsolve` to do that. More precisely, we want to solve the equation $f(x) = \cos(x) = 0$. We create a function that defines that equation, and then use `scipy.optimize.fsolve` to solve it.

```
from scipy.optimize import fsolve
import numpy as np

def f(x):
    return np.cos(x)

sol, = fsolve(f, x0=1.5) # the comma after sol makes it return a float
print sol
print np.pi / 2
```

```
1.57079632679
1.57079632679
```

We know the solution is $\pi/2$.

2.7 Advanced function creation

Python has some nice features in creating functions. You can create default values for variables, have optional variables and optional keyword variables. In this function f(a,b), `a` and `b` are called positional arguments, and they are required, and must be provided in the same order as the function defines.

If we provide a default value for an argument, then the argument is called a keyword argument, and it becomes optional. You can combine positional arguments and keyword arguments, but positional arguments must come first. Here is an example.

```
def func(a, n=2):
    "compute the nth power of a"
    return a**n

# three different ways to call the function
print func(2)
print func(2, 3)
print func(2, n=4)
```

```
4
8
16
```

In the first call to the function, we only define the argument `a`, which is a mandatory, positional argument. In the second call, we define `a` and `n`, in the order they are defined in the function. Finally, in the third call, we define `a` as a positional argument, and `n` as a keyword argument.

If all of the arguments are optional, we can even call the function with no arguments. If you give arguments as positional arguments, they are used in the order defined in the function. If you use keyword arguments, the order is arbitrary.

```
def func(a=1, n=2):
    "compute the nth power of a"
    return a**n

# three different ways to call the function
print func()
print func(2, 4)
print func(n=4, a=2)
```

```
1
16
16
```

It is occasionally useful to allow an arbitrary number of arguments in a function. Suppose we want a function that can take an arbitrary number of positional arguments and return the sum of all the arguments. We use the syntax `*args` to indicate arbitrary positional arguments. Inside the function the variable `args` is a tuple containing all of the arguments passed to the function.

```
def func(*args):
    sum = 0
    for arg in args:
        sum += arg
    return sum

print func(1, 2, 3, 4)
```

```
10
```

A more "functional programming" version of the last function is given here. This is an advanced approach that is less readable to new users, but more compact and likely more efficient for large numbers of arguments.

```
import operator
def func(*args):
    return reduce(operator.add, args)
print func(1, 2, 3, 4)
```

```
10
```

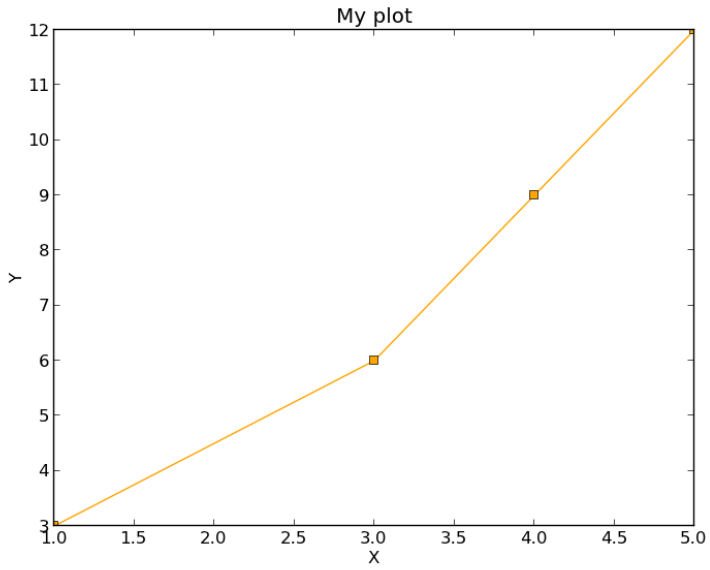
It is possible to have arbitrary keyword arguments. This is a common pattern when you call another function within your function that takes keyword arguments. We use `**kwargs` to indicate that arbitrary keyword arguments can be given to the function. Inside the function, kwargs is variable containing a dictionary of the keywords and values passed in.

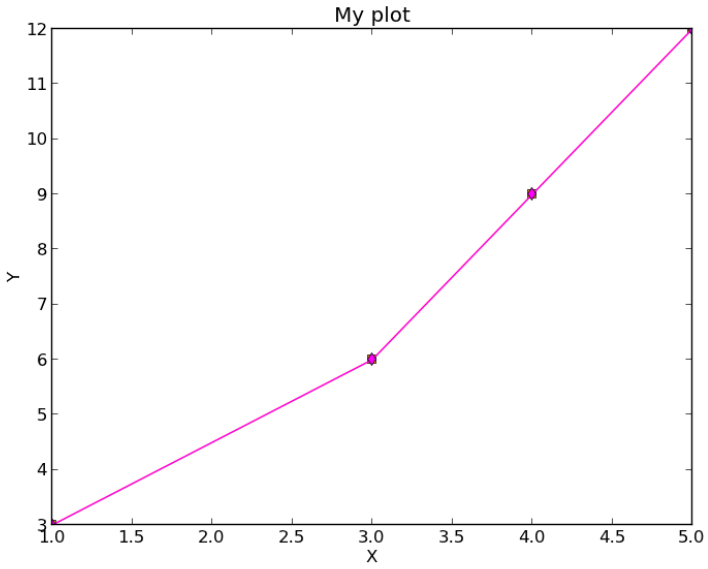
```
def func(**kwargs):
    for kw in kwargs:
        print '{0} = {1}'.format(kw, kwargs[kw])

func(t1=6, color='blue')
```

```
color = blue
t1 = 6
```

A typical example might be:

```
import matplotlib.pyplot as plt

def myplot(x, y, fname=None, **kwargs):
    "make plot of x,y. save to fname if not None. provide kwargs to plot"
    plt.plot(x, y, **kwargs)
    plt.xlabel('X')
    plt.ylabel('Y')
    plt.title('My plot')
    if fname:
        plt.savefig(fname)
    else:
        plt.show()

x = [1, 3, 4, 5]
y = [3, 6, 9, 12]

myplot(x, y, 'images/myfig.png', color='orange', marker='s')

# you can use a dictionary as kwargs
d = {'color':'magenta',
     'marker':'d'}

myplot(x, y, 'images/myfig2.png', **d)
```





In that example we wrap the matplotlib plotting commands in a function, which we can call the way we want to, with arbitrary optional arguments. In this example, you cannot pass keyword arguments that are illegal to the plot command or you will get an error.

It is possible to combine all the options at once. I admit it is hard to imagine where this would be really useful, but it can be done!

```
import numpy as np

def func(a, b=2, *args, **kwargs):
    "return a**b + sum(args) and print kwargs"
    for kw in kwargs:
        print 'kw: {0} = {1}'.format(kw, kwargs[kw])

    return a**b + np.sum(args)

print func(2, 3, 4, 5, mysillykw='hahah')
```

```
kw: mysillykw = hahah
17
```

2.8 Controlling the format of printed variables

This was first worked out in this original Matlab post.

Often you will want to control the way a variable is printed. You may want to only show a few decimal places, or print in scientific notation, or embed the result in a string. Here are some examples of printing with no control over the format.

```
a = 2./3
print a
print 1/3
print 1./3.
print 10.1
print "Avogadro's number is ", 6.022e23,'.'
```

```
0.666666666667
0
0.333333333333
10.1
Avogadro's number is  6.022e+23 .
```

There is no control over the number of decimals, or spaces around a printed number.

In python, we use the format function to control how variables are printed. With the format function you use codes like {n:format specifier} to indicate that a formatted string should be used. n is the $n\hat{}th$ argument passed to format, and there are a variety of format specifiers. Here we examine how to format float numbers. The specifier has the general form "w.df" where w is the width of the field, and d is the number of decimals, and f indicates a float number. "1.3f" means to print a float number with 3 decimal places. Here is an example.

```
print 'The value of 1/3 to 3 decimal places is {0:1.3f}'.format(1./3.)
```

```
The value of 1/3 to 3 decimal places is 0.333
```

In that example, the 0 in {0:1.3f} refers to the first (and only) argument to the format function. If there is more than one argument, we can refer to them like this:

```
print 'Value 0 = {0:1.3f}, value 1 = {1:1.3f}, value 0 = {0:1.3f}'.format(1./3., 1./6.)
```

```
Value 0 = 0.333, value 1 = 0.167, value 0 = 0.333
```

Note you can refer to the same argument more than once, and in arbitrary order within the string.

Suppose you have a list of numbers you want to print out, like this:

```
for x in [1./3., 1./6., 1./9.]:
    print 'The answer is {0:1.2f}'.format(x)
```

```
The answer is 0.33
The answer is 0.17
The answer is 0.11
```

The “g” format specifier is a general format that can be used to indicate a precision, or to indicate significant digits. To print a number with a specific number of significant digits we do this:

```
print '{0:1.3g}'.format(1./3.)
print '{0:1.3g}'.format(4./3.)
```

```
0.333
1.33
```

We can also specify plus or minus signs. Compare the next two outputs.

```
for x in [-1., 1.]:
    print '{0:1.2f}'.format(x)
```

```
-1.00
1.00
```

You can see the decimals do not align. That is because there is a minus sign in front of one number. We can specify to show the sign for positive and negative numbers, or to pad positive numbers to leave space for positive numbers.

```
for x in [-1., 1.]:
    print '{0:+1.2f}'.format(x) # explicit sign

for x in [-1., 1.]:
    print '{0: 1.2f}'.format(x) # pad positive numbers
```

```
-1.00
+1.00
-1.00
 1.00
```

We use the “e” or “E” format modifier to specify scientific notation.

```
import numpy as np
eps = np.finfo(np.double).eps
print eps
print '{0}'.format(eps)
print '{0:1.2f}'.format(eps)
print '{0:1.2e}'.format(eps)  #exponential notation
print '{0:1.2E}'.format(eps)  #exponential notation with capital E
```

```
2.22044604925e-16
2.22044604925e-16
0.00
2.22e-16
2.2E-16
```

As a float with 2 decimal places, that very small number is practically equal to 0.

We can even format percentages. Note you do not need to put the % in your string.

```
print 'the fraction {0} corresponds to {0:1.0%}'.format(0.78)
```

```
the fraction 0.78 corresponds to 78%
```

There are many other options for formatting strings. See http://docs.python.org/2/library/string.html#form for a full specification of the options.

2.9 Advanced string formatting

There are several more advanced ways to include formatted values in a string. In the previous case we examined replacing format specifiers by *positional* arguments in the format command. We can instead use *keyword* arguments.

```
s = 'The {speed} {color} fox'.format(color='brown', speed='quick')
print s
```

```
The quick brown fox
```

If you have a lot of variables already defined in a script, it is convenient to use them in string formatting with the locals command:

```
speed = 'slow'
color= 'blue'

print 'The {speed} {color} fox'.format(**locals())
```

```
The slow blue fox
```

If you want to access attributes on an object, you can specify them directly in the format identifier.

```
class A:
    def __init__(self, a, b, c):
        self.a = a
        self.b = b
        self.c = c

mya = A(3,4,5)

print 'a = {obj.a}, b = {obj.b}, c = {obj.c:1.2f}'.format(obj=mya)
```

```
a = 3, b = 4, c = 5.00
```

You can access values of a dictionary:

```
d = {'a': 56, "test":'woohoo!'}

print "the value of a in the dictionary is {obj[a]}. It works {obj[test]}".format(obj=d)
```

```
the value of a in the dictionary is 56. It works woohoo!.
```

And, you can access elements of a list. Note, however you cannot use -1 as an index in this case.

```
L = [4, 5, 'cat']

print 'element 0 = {obj[0]}, and the last element is {obj[2]}'.format(obj=L)
```

```
element 0 = 4, and the last element is cat
```

There are three different ways to "print" an object. If an object has a __format__ function, that is the default used in the format command. It may be helpful to use the `str` or `repr` of an object instead. We get this with !s for `str` and !r for `repr`.

```
class A:
    def __init__(self, a, b):
        self.a = a; self.b = b

    def __format__(self, format):
        s = 'a={{0:{0}}} b={{1:{0}}}'.format(format)
        return s.format(self.a, self.b)

    def __str__(self):
        return 'str: class A, a={0} b={1}'.format(self.a, self.b)

    def __repr__(self):
        return 'representing: class A, a={0}, b={1}'.format(self.a, self.b)

mya = A(3, 4)

print '{0}'.format(mya)   # uses __format__
print '{0!s}'.format(mya) # uses __str__
print '{0!r}'.format(mya) # uses __repr__
```

```
a=3 b=4
str: class A, a=3 b=4
representing: class A, a=3, b=4
```

This covers the majority of string formatting requirements I have come across. If there are more sophisticated needs, they can be met with various string templating python modules. the one I have used most is Cheetah.

2.10 Indexing vectors and arrays in Python

Matlab post There are times where you have a lot of data in a vector or array and you want to extract a portion of the data for some analysis. For example,

maybe you want to plot column 1 vs column 2, or you want the integral of data between x = 4 and x = 6, but your vector covers 0 ¡ x ¡ 10. Indexing is the way to do these things.

A key point to remember is that in python array/vector indices start at 0. Unlike Matlab, which uses parentheses to index a array, we use brackets in python.

```
import numpy as np

x = np.linspace(-np.pi, np.pi, 10)
print x

print x[0]  # first element
print x[2]  # third element
print x[-1] # last element
print x[-2] # second to last element
```

```
>>> >>> [-3.14159265 -2.44346095 -1.74532925 -1.04719755 -0.34906585  0.34906585
  1.04719755  1.74532925  2.44346095  3.14159265]
>>> -3.14159265359
-1.74532925199
3.14159265359
2.44346095279
```

We can select a range of elements too. The syntax a:b extracts the aˆth to (b-1)ˆth elements. The syntax a:b:n starts at a, skips nelements up to the index b.

```
print x[1:4]     # second to fourth element. Element 5 is not included
print x[0:-1:2]  # every other element
print x[:]       # print the whole vector
print x[-1:0:-1] # reverse the vector!
```

```
[-2.44346095 -1.74532925 -1.04719755]
[-3.14159265 -1.74532925 -0.34906585  1.04719755  2.44346095]
[-3.14159265 -2.44346095 -1.74532925 -1.04719755 -0.34906585  0.34906585
  1.04719755  1.74532925  2.44346095  3.14159265]
[ 3.14159265  2.44346095  1.74532925  1.04719755  0.34906585 -0.34906585
 -1.04719755 -1.74532925 -2.44346095]
```

Suppose we want the part of the vector where x ¿ 2. We could do that by inspection, but there is a better way. We can create a mask of boolean (0 or 1) values that specify whether x ¿ 2 or not, and then use the mask as an index.

```
print x[x > 2]
```

```
[ 2.44346095  3.14159265]
```

You can use this to analyze subsections of data, for example to integrate the function y = sin(x) where x ¿ 2.

```
y = np.sin(x)

print np.trapz( x[x > 2], y[x > 2])
```

```
>>> -1.79500162881
```

2.10.1 2d arrays

In 2d arrays, we use row, column notation. We use a : to indicate all rows or all columns.

```
a = np.array([[1, 2, 3],
              [4, 5, 6],
              [7, 8, 9]])

print a[0, 0]
print a[-1, -1]

print a[0, :] # row one
print a[:, 0] # column one
print a[:]
```

```
... >>> >>> 1
9
>>> [1 2 3]
[1 4 7]
[[1 2 3]
 [4 5 6]
 [7 8 9]]
```

2.10.2 Using indexing to assign values to rows and columns

```
b = np.zeros((3, 3))
print b

b[:, 0] = [1, 2, 3] # set column 0
b[2, 2] = 12        # set a single element
print b

b[2] = 6  # sets everything in row 2 to 6!
print b
```

```
[[ 0.  0.  0.]
 [ 0.  0.  0.]
 [ 0.  0.  0.]]
>>> >>> >>> [[  1.   0.   0.]
```

```
 [  2.   0.   0.]
 [  3.   0.  12.]]
>>> >>> [[ 1.  0.  0.]
 [ 2.  0.  0.]
 [ 6.  6.  6.]]
```

Python does not have the linear assignment method like Matlab does. You can achieve something like that as follows. We flatten the array to 1D, do the linear assignment, and reshape the result back to the 2D array.

```
c = b.flatten()
c[2] = 34
b[:] = c.reshape(b.shape)
print b
```

```
 >>> >>> [[  1.   0.  34.]
  [  2.   0.   0.]
  [  6.   6.   6.]]
```

2.10.3 3D arrays

The 3d array is like book of 2D matrices. Each page has a 2D matrix on it. think about the indexing like this: (row, column, page)

```
M = np.random.uniform(size=(3,3,3))  # a 3x3x3 array
print M
```

```
[[[ 0.78557795  0.36454381  0.96090072]
  [ 0.76133373  0.03250485  0.08517174]
  [ 0.96007909  0.08654002  0.29693648]]

 [[ 0.58270738  0.60656083  0.47703339]
  [ 0.62551477  0.62244626  0.11030327]
  [ 0.2048839   0.83081982  0.83660668]]

 [[ 0.12489176  0.20783996  0.38481792]
  [ 0.05234762  0.03989146  0.09731516]
  [ 0.67427208  0.51793637  0.89016255]]]
```

```
print M[:, :, 0]  # 2d array on page 0
print M[:, 0, 0]  # column 0 on page 0
print M[1, :, 2]  # row 1 on page 2
```

```
 [[ 0.78557795  0.76133373  0.96007909]
  [ 0.58270738  0.62551477  0.2048839 ]
  [ 0.12489176  0.05234762  0.67427208]]
 [ 0.78557795  0.58270738  0.12489176]
 [ 0.47703339  0.11030327  0.83660668]
```

2.10.4 Summary

The most common place to use indexing is probably when a function returns an array with the independent variable in column 1 and solution in column 2, and you want to plot the solution. Second is when you want to analyze one part of the solution. There are also applications in numerical methods, for example in assigning values to the elements of a matrix or vector.

2.11 Creating arrays in python

Often, we will have a set of 1-D arrays, and we would like to construct a 2D array with those vectors as either the rows or columns of the array. This may happen because we have data from different sources we want to combine, or because we organize the code with variables that are easy to read, and then want to combine the variables. Here are examples of doing that to get the vectors as the columns.

```
import numpy as np

a = np.array([1, 2, 3])
b = np.array([4, 5, 6])

print np.column_stack([a, b])

# this means stack the arrays vertically, e.g. on top of each other
print np.vstack([a, b]).T
```

```
 [[1 4]
  [2 5]
  [3 6]]
 [[1 4]
  [2 5]
  [3 6]]
```

Or rows:

```
import numpy as np

a = np.array([1, 2, 3])
b = np.array([4, 5, 6])

print np.row_stack([a, b])

# this means stack the arrays vertically, e.g. on top of each other
print np.vstack([a, b])
```

```
 [[1 2 3]
  [4 5 6]]
 [[1 2 3]
  [4 5 6]]
```

The opposite operation is to extract the rows or columns of a 2D array into smaller arrays. We might want to do that to extract a row or column from a calculation for further analysis, or plotting for example. There are splitting functions in numpy. They are somewhat confusing, so we examine some examples. The numpy.hsplit command splits an array "horizontally". The best way to think about it is that the "splits" move horizontally across the array. In other words, you draw a vertical split, move over horizontally, draw another vertical split, etc... You must specify the number of splits that you want, and the array must be evenly divisible by the number of splits.

```
import numpy as np

A = np.array([[1, 2, 3, 5],
              [4, 5, 6, 9]])

# split into two parts
p1, p2 = np.hsplit(A, 2)
print p1
print p2

#split into 4 parts
p1, p2, p3, p4 = np.hsplit(A, 4)
print p1
print p2
print p3
print p4
```

```
[[1 2]
 [4 5]]
[[3 5]
 [6 9]]
[[1]
 [4]]
[[2]
 [5]]
[[3]
 [6]]
[[5]
 [9]]
```

In the numpy.vsplit command the "splits" go "vertically" down the array. Note that the split commands return 2D arrays.

```
import numpy as np

A = np.array([[1, 2, 3, 5],
              [4, 5, 6, 9]])

# split into two parts
p1, p2 = np.vsplit(A, 2)
print p1
print p2
print p2.shape
```

```
[[1 2 3 5]]
[[4 5 6 9]]
(1, 4)
```

An alternative approach is array unpacking. In this example, we unpack the array into two variables. The array unpacks by row.

```
import numpy as np

A = np.array([[1, 2, 3, 5],
              [4, 5, 6, 9]])

# split into two parts
p1, p2 = A
print p1
print p2
```

```
[1 2 3 5]
[4 5 6 9]
```

To get the columns, just transpose the array.

```
import numpy as np

A = np.array([[1, 2, 3, 5],
              [4, 5, 6, 9]])

# split into two parts
p1, p2, p3, p4 = A.T
print p1
print p2
print p3
print p4
print p4.shape
```

```
[1 4]
[2 5]
[3 6]
[5 9]
(2,)
```

Note that now, we have 1D arrays.

You can also access rows and columns by indexing. We index an array by [row, column]. To get a row, we specify the row number, and all the columns in that row like this [row, :]. Similarly, to get a column, we specify that we want all rows in that column like this: [:, column]. This approach is useful when you only want a few columns or rows.

```
import numpy as np

A = np.array([[1, 2, 3, 5],
              [4, 5, 6, 9]])

# get row 1
```

```
print A[1]
print A[1, :]  # row 1, all columns

print A[:, 2]  # get third column
print A[:, 2].shape
```

```
[4 5 6 9]
[4 5 6 9]
[3 6]
(2,)
```

Note that even when we specify a column, it is returned as a 1D array.

3 Math

3.1 Numeric derivatives by differences

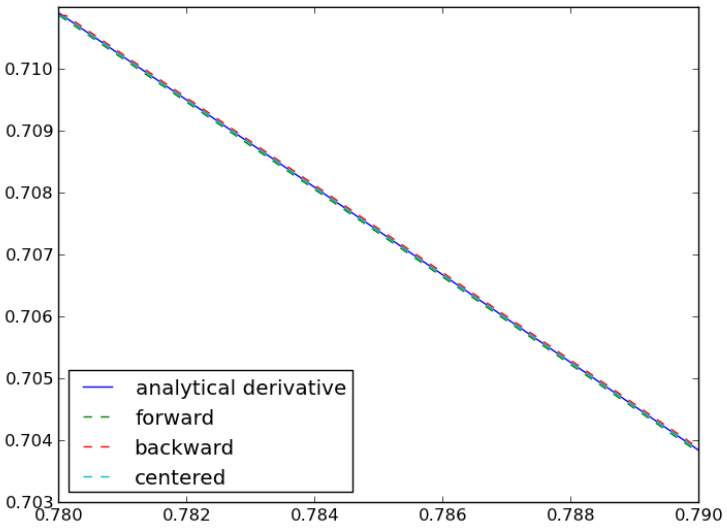
numpy has a function called numpy.diff() that is similar to the one found in matlab. It calculates the differences between the elements in your list, and returns a list that is one element shorter, which makes it unsuitable for plotting the derivative of a function.

Loops in python are pretty slow (relatively speaking) but they are usually trivial to understand. In this script we show some simple ways to construct derivative vectors using loops. It is implied in these formulas that the data points are equally spaced. If they are not evenly spaced, you need a different approach.

```
import numpy as np
from pylab import *
import time

'''
These are the brainless way to calculate numerical derivatives. They
work well for very smooth data. they are surprisingly fast even up to
10000 points in the vector.
'''

x = np.linspace(0.78,0.79,100)
y = np.sin(x)
dy_analytical = np.cos(x)
'''
lets use a forward difference method:
that works up until the last point, where there is not
a forward difference to use. there, we use a backward difference.
'''

tf1 = time.time()
dyf = [0.0]*len(x)
for i in range(len(y)-1):
    dyf[i] = (y[i+1] - y[i])/(x[i+1]-x[i])
#set last element by backwards difference
dyf[-1] = (y[-1] - y[-2])/(x[-1] - x[-2])

print ' Forward difference took %1.1f seconds' % (time.time() - tf1)

'''and now a backwards difference'''
```

```
tb1 = time.time()
dyb = [0.0]*len(x)
#set first element by forward difference
dyb[0] = (y[0] - y[1])/(x[0] - x[1])
for i in range(1,len(y)):
    dyb[i] = (y[i] - y[i-1])/(x[i]-x[i-1])

print ' Backward difference took %1.1f seconds' % (time.time() - tb1)

'''and now, a centered formula'''
tc1 = time.time()
dyc = [0.0]*len(x)
dyc[0] = (y[0] - y[1])/(x[0] - x[1])
for i in range(1,len(y)-1):
    dyc[i] = (y[i+1] - y[i-1])/(x[i+1]-x[i-1])
dyc[-1] = (y[-1] - y[-2])/(x[-1] - x[-2])

print ' Centered difference took %1.1f seconds' % (time.time() - tc1)

'''
the centered formula is the most accurate formula here
'''

plt.plot(x,dy_analytical,label='analytical derivative')
plt.plot(x,dyf,'--',label='forward')
plt.plot(x,dyb,'--',label='backward')
plt.plot(x,dyc,'--',label='centered')

plt.legend(loc='lower left')
plt.savefig('images/simple-diffs.png')
plt.show()
```

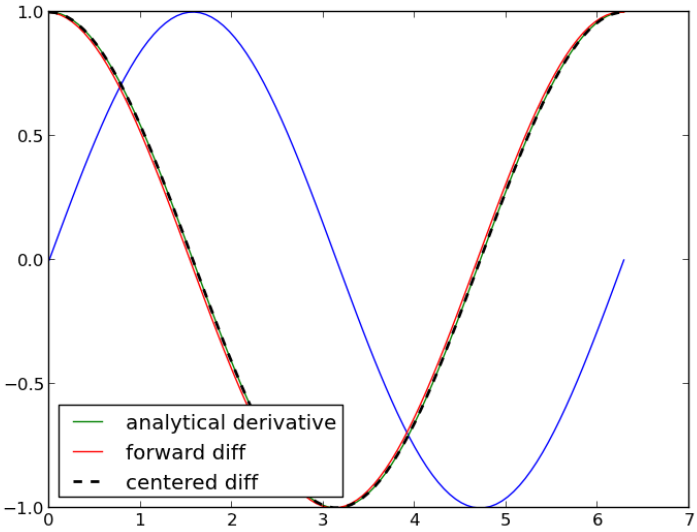
```
Forward difference took 0.0 seconds
Backward difference took 0.0 seconds
Centered difference took 0.0 seconds
```



3.2 Vectorized numeric derivatives

Loops are usually not great for performance. Numpy offers some vectorized methods that allow us to compute derivatives without loops, although this comes at the mental cost of harder to understand syntax

```
import numpy as np
import matplotlib.pyplot as plt

x = np.linspace(0, 2 * np.pi, 100)
y = np.sin(x)
dy_analytical = np.cos(x)


# we need to specify the size of dy ahead because diff returns
#an array of n-1 elements
dy = np.zeros(y.shape, np.float) #we know it will be this size
dy[0:-1] = np.diff(y) / np.diff(x)
dy[-1] = (y[-1] - y[-2]) / (x[-1] - x[-2])


'''
calculate dy by center differencing using array slices
'''

dy2 = np.zeros(y.shape,np.float) #we know it will be this size
dy2[1:-1] = (y[2:] - y[0:-2]) / (x[2:] - x[0:-2])

# now the end points
dy2[0] = (y[1] - y[0]) / (x[1] - x[0])
dy2[-1] = (y[-1] - y[-2]) / (x[-1] - x[-2])

plt.plot(x,y)
plt.plot(x,dy_analytical,label='analytical derivative')
plt.plot(x,dy,label='forward diff')
plt.plot(x,dy2,'k--',lw=2,label='centered diff')
plt.legend(loc='lower left')
plt.savefig('images/vectorized-diffs.png')
plt.show()
```



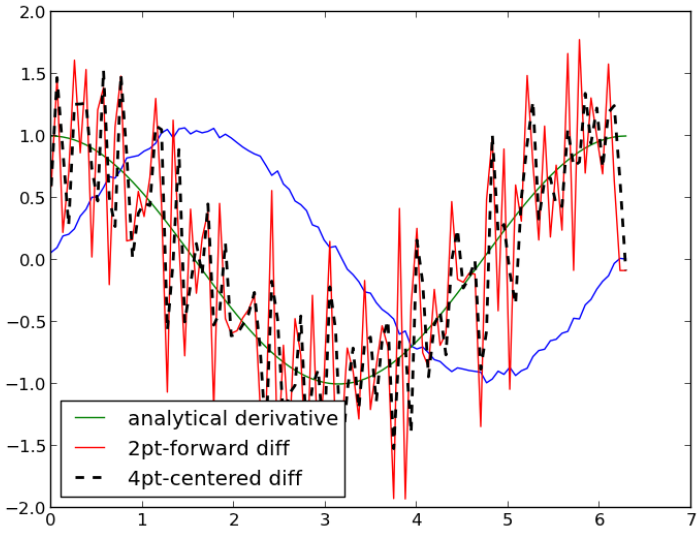
3.3 2-point vs. 4-point numerical derivatives

If your data is very noisy, you will have a hard time getting good derivatives; derivatives tend to magnify noise. In these cases, you have to employ smoothing techniques, either implicitly by using a multipoint derivative formula, or explicitly by smoothing the data yourself, or taking the derivative of a function that has been fit to the data in the neighborhood you are interested in.

Here is an example of a 4-point centered difference of some noisy data:

```
import numpy as np
import matplotlib.pyplot as plt

x = np.linspace(0, 2*np.pi, 100)
y = np.sin(x) + 0.1 * np.random.random(size=x.shape)
dy_analytical = np.cos(x)

#2-point formula
dyf = [0.0] * len(x)
for i in range(len(y)-1):
    dyf[i] = (y[i+1] - y[i])/(x[i+1]-x[i])
#set last element by backwards difference
dyf[-1] = (y[-1] - y[-2])/(x[-1] - x[-2])

'''
calculate dy by 4-point center differencing using array slices

\frac{y[i-2] - 8y[i-1] + 8[i+1] - y[i+2]}{12h}

y[0] and y[1] must be defined by lower order methods
and y[-1] and y[-2] must be defined by lower order methods
'''

dy = np.zeros(y.shape, np.float) #we know it will be this size
```

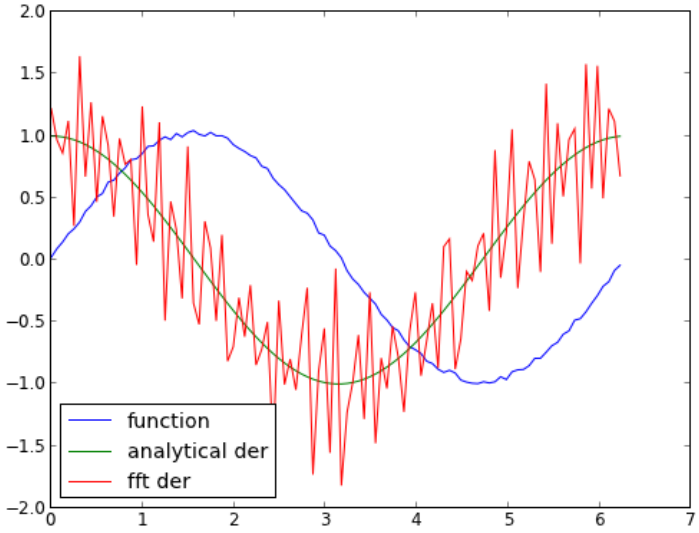
```
h = x[1] - x[0] #this assumes the points are evenely spaced!
dy[2:-2] = (y[0:-4] - 8 * y[1:-3] + 8 * y[3:-1] - y[4:]) / (12.0 * h)

# simple differences at the end-points
dy[0] = (y[1] - y[0])/(x[1] - x[0])
dy[1] = (y[2] - y[1])/(x[2] - x[1])
dy[-2] = (y[-2] - y[-3]) / (x[-2] - x[-3])
dy[-1] = (y[-1] - y[-2]) / (x[-1] - x[-2])


plt.plot(x, y)
plt.plot(x, dy_analytical, label='analytical derivative')
plt.plot(x, dyf, 'r-', label='2pt-forward diff')
plt.plot(x, dy, 'k--', lw=2, label='4pt-centered diff')
plt.legend(loc='lower left')
plt.savefig('images/multipt-diff.png')
plt.show()
```



3.4 Derivatives by FFT

```
import numpy as np
import matplotlib.pyplot as plt

N = 101 #number of points
L = 2 * np.pi #interval of data

x = np.arange(0.0, L, L/float(N)) #this does not include the endpoint

#add some random noise
y = np.sin(x) + 0.05 * np.random.random(size=x.shape)
dy_analytical = np.cos(x)

'''
http://sci.tech-archive.net/Archive/sci.math/2008-05/msg00401.html

```

```
you can use fft to calculate derivatives!
'''

if N % 2 == 0:
    k = np.asarray(range(0, N / 2) + [0] + range(-N / 2 + 1,0))
else:
    k = np.asarray(range(0,(N - 1) / 2) + [0] + range(-(N - 1) / 2, 0))

k *= 2 * np.pi / L

fd = np.real(np.fft.ifft(1.0j * k * np.fft.fft(y)))

plt.plot(x, y, label='function')
plt.plot(x,dy_analytical,label='analytical der')
plt.plot(x,fd,label='fft der')
plt.legend(loc='lower left')

plt.savefig('images/fft-der.png')
plt.show()
```



3.5 A novel way to numerically estimate the derivative of a function - complex-step derivative approximation

Matlab post

Adapted from http://biomedicalcomputationreview.org/2/3/8.pdf and http://dl.acm.org/citation.cfm?id=8

This posts introduces a novel way to numerically estimate the derivative of a function that does not involve finite difference schemes. Finite difference schemes are approximations to derivatives that become more and more accurate as the step size goes to zero, except that as the step size approaches the limits of machine accuracy, new errors can appear in the approximated results. In the

references above, a new way to compute the derivative is presented that does not rely on differences!

The new way is: $f'(x) = \text{imag}(\text{f}(\text{x} + \text{i}\Delta\text{x})/\Delta\text{x})$ where the function f is evaluated in imaginary space with a small Δx in the complex plane. The derivative is miraculously equal to the imaginary part of the result in the limit of $\$\Delta$ x $\rightarrow$ 0$!

This example comes from the first link. The derivative must be evaluated using the chain rule. We compare a forward difference, central difference and complex-step derivative approximations.

```
import numpy as np
import matplotlib.pyplot as plt

def f(x):   return np.sin(3*x)*np.log(x)

x = 0.7
h = 1e-7

# analytical derivative
dfdx_a = 3 * np.cos( 3*x)*np.log(x) + np.sin(3*x) / x

# finite difference
dfdx_fd = (f(x + h) - f(x))/h

# central difference
dfdx_cd = (f(x+h)-f(x-h))/(2*h)

# complex method
dfdx_I = np.imag(f(x + np.complex(0, h))/h)

print dfdx_a
print dfdx_fd
print dfdx_cd
print dfdx_cd
```

```
1.77335410624
1.7733539398
1.77335410523
1.77335410523
```

These are all the same to 4 decimal places. The simple finite difference is the least accurate, and the central differences is practically the same as the complex number approach.

Let us use this method to verify the fundamental Theorem of Calculus, i.e. to evaluate the derivative of an integral function. Let $f(x) = \int_1^{x^2} tan(t^3)dt$, and we now want to compute df/dx. Of course, this can be done analytically, but it is not trivial!

```
import numpy as np
from scipy.integrate import quad

def f_(z):
    def integrand(t):
        return np.tan(t**3)
```

```
    return quad(integrand, 0, z**2)

f = np.vectorize(f_)

x = np.linspace(0, 1)

h = 1e-7

dfdx = np.imag(f(x + complex(0, h)))/h
dfdx_analytical = 2 * x * np.tan(x**6)

import matplotlib.pyplot as plt

plt.plot(x, dfdx, x, dfdx_analytical, 'r--')
plt.show()
```

```
>>> >>> ... ... ... ... >>> >>> >>> >>> >>> >>> >>> c:\Python27\lib\site-packages\scipy\inte
  return _quadpack._qagse(func,a,b,args,full_output,epsabs,epsrel,limit)
Traceback (most recent call last):
  File "<stdin>", line 1, in <module>
  File "c:\Python27\lib\site-packages\numpy\lib\function_base.py", line 1885, in __call__
    for x, c in zip(self.ufunc(*newargs), self.otypes)])
  File "<stdin>", line 4, in f_
  File "c:\Python27\lib\site-packages\scipy\integrate\quadpack.py", line 247, in quad
    retval = _quad(func,a,b,args,full_output,epsabs,epsrel,limit,points)
  File "c:\Python27\lib\site-packages\scipy\integrate\quadpack.py", line 312, in _quad
    return _quadpack._qagse(func,a,b,args,full_output,epsabs,epsrel,limit)
TypeError: can't convert complex to float
>>> >>> >>> >>> Traceback (most recent call last):
  File "<stdin>", line 1, in <module>
NameError: name 'dfdx' is not defined
```

Interesting this fails.

3.6 derivatives by polynomial fitting

3.7 derivatives by fitting

3.8 Vectorized piecewise functions

Matlab post Occasionally we need to define piecewise functions, e.g.

$$\begin{aligned} f(x) &= 0, x < 0 && (1)\\ &= x, 0 <= x < 1 && (2)\\ &= 2 - x, 1 < x <= 2 && (3)\\ &= 0, x > 2 && (4) \end{aligned}$$

Today we examine a few ways to define a function like this. A simple way is to use conditional statements.

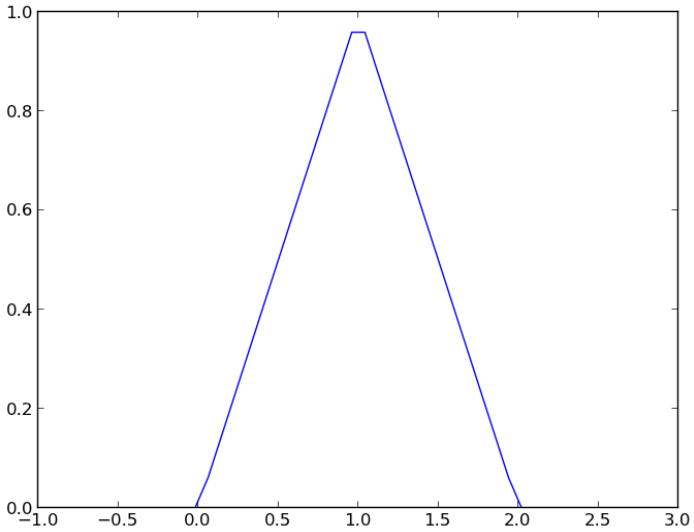
```
def f1(x):
    if x < 0:
        return 0
    elif (x >= 0) & (x < 1):
        return x
    elif (x >= 1) & (x < 2):
        return 2.0 - x
    else:
        return 0

print f1(-1)
print f1([0, 1, 2, 3])  # does not work!
```

```
... ... ... ... ... ... ... ... >>> 0
0
```

This works, but the function is not vectorized, i.e. f([-1 0 2 3]) does not evaluate properly (it should give a list or array). You can get vectorized behavior by using list comprehension, or by writing your own loop. This does not fix all limitations, for example you cannot use the f1 function in the quad function to integrate it.

```
import numpy as np
import matplotlib.pyplot as plt

x = np.linspace(-1, 3)
y = [f1(xx) for xx in x]

plt.plot(x, y)
plt.savefig('images/vector-piecewise.png')
```

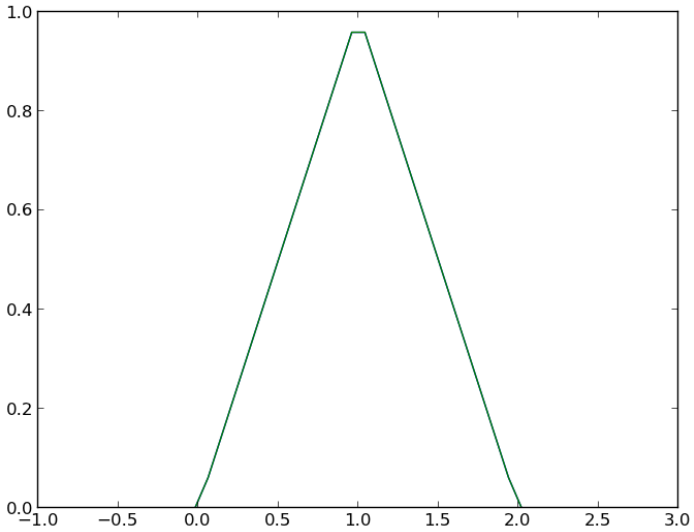
```
>>> >>> >>> >>> >>> [<matplotlib.lines.Line2D object at 0x048D6790>]
```



Neither of those methods is convenient. It would be nicer if the function was vectorized, which would allow the direct notation f1([0, 1, 2, 3, 4]). A simple way to achieve this is through the use of logical arrays. We create logical arrays from comparison statements.

```
def f2(x):
    'fully vectorized version'
    x = np.asarray(x)
    y = np.zeros(x.shape)
    y += ((x >= 0) & (x < 1)) * x
    y += ((x >= 1) & (x < 2)) * (2 - x)
    return y

print f2([-1, 0, 1, 2, 3, 4])
x = np.linspace(-1,3);
plt.plot(x,f2(x))
plt.savefig('images/vector-piecewise-2.png')
```

```
... ... ... ... ... ... >>> [ 0.  0.  1.  0.  0.  0.]
>>> [<matplotlib.lines.Line2D object at 0x043A4910>]
```



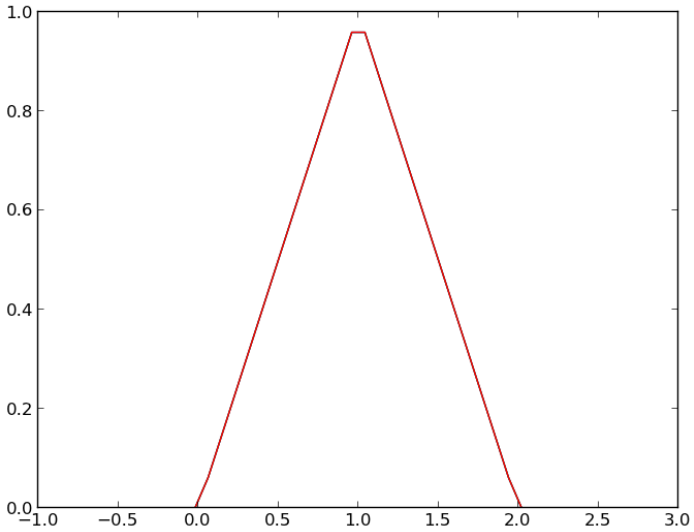
A third approach is to use Heaviside functions. The Heaviside function is defined to be zero for x less than some value, and 0.5 for x=0, and 1 for x ¿= 0. If you can live with y=0.5 for x=0, you can define a vectorized function in terms of Heaviside functions like this.

```
def heaviside(x):
    x = np.array(x)
    if x.shape != ():
        y = np.zeros(x.shape)
        y[x > 0.0] = 1
        y[x == 0.0] = 0.5
    else: # special case for 0d array (a number)
        if x > 0: y = 1
        elif x == 0: y = 0.5
        else: y = 0
    return y

def f3(x):
    x = np.array(x)
    y1 = (heaviside(x) - heaviside(x - 1)) * x # first interval
    y2 = (heaviside(x - 1) - heaviside(x - 2)) * (2 - x) # second interval
    return y1 + y2

from scipy.integrate import quad
print quad(f3, -1, 3)
```

```
... ... ... ... ... ... ... ... ... ... >>> ... ... ... ... ... >>> >>> (1.0, 1.11022302462
```

```
plt.plot(x, f3(x))
plt.savefig('images/vector-piecewise-3.png')
```

```
[<matplotlib.lines.Line2D object at 0x048F96F0>]
```



There are many ways to define piecewise functions, and vectorization is not always necessary. The advantages of vectorization are usually notational simplicity and speed; loops in python are usually very slow compared to vectorized functions.

3.9 Smooth transitions between discontinuous functions

original post

In Post 1280 we used a correlation for the Fanning friction factor for turbulent flow in a pipe. For laminar flow (Re ¡ 3000), there is another correlation that is commonly used: $f_F = 16/Re$. Unfortunately, the correlations for laminar flow and turbulent flow have different values at the transition that should occur at Re = 3000. This discontinuity can cause a lot of problems for numerical solvers that rely on derivatives.

Today we examine a strategy for smoothly joining these two functions. First we define the two functions.

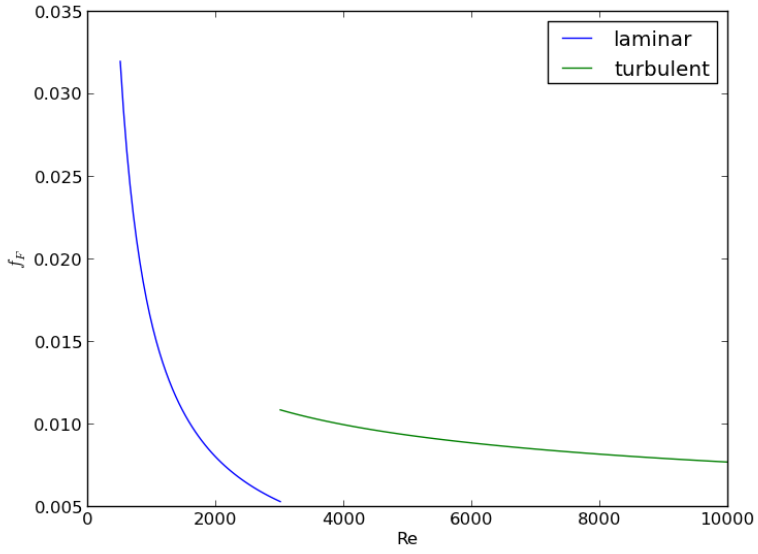
```
import numpy as np
from scipy.optimize import fsolve
import matplotlib.pyplot as plt

def fF_laminar(Re):
    return 16.0 / Re

def fF_turbulent_unvectorized(Re):
    # Nikuradse correlation for turbulent flow
    # 1/np.sqrt(f) = (4.0*np.log10(Re*np.sqrt(f))-0.4)
    # we have to solve this equation to get f
    def func(f):
        return 1/np.sqrt(f) - (4.0*np.log10(Re*np.sqrt(f))-0.4)
    fguess = 0.01
```

```
    f, = fsolve(func, fguess)
    return f

# this enables us to pass vectors to the function and get vectors as
# solutions
fF_turbulent = np.vectorize(fF_turbulent_unvectorized)
```

Now we plot the correlations.

```
Re1 = np.linspace(500, 3000)
f1 = fF_laminar(Re1)

Re2 = np.linspace(3000, 10000)
f2 = fF_turbulent(Re2)

plt.figure(1); plt.clf()
plt.plot(Re1, f1, label='laminar')
plt.plot(Re2, f2, label='turbulent')
plt.xlabel('Re')
plt.ylabel('$f_F$')
plt.legend()
plt.savefig('images/smooth-transitions-1.png')
```

```
>>> >>> >>> >>> >>> <matplotlib.figure.Figure object at 0x051FF630>
[<matplotlib.lines.Line2D object at 0x05963C10>]
[<matplotlib.lines.Line2D object at 0x0576DD70>]
<matplotlib.text.Text object at 0x0577CFF0>
<matplotlib.text.Text object at 0x05798790>
<matplotlib.legend.Legend object at 0x05798030>
```

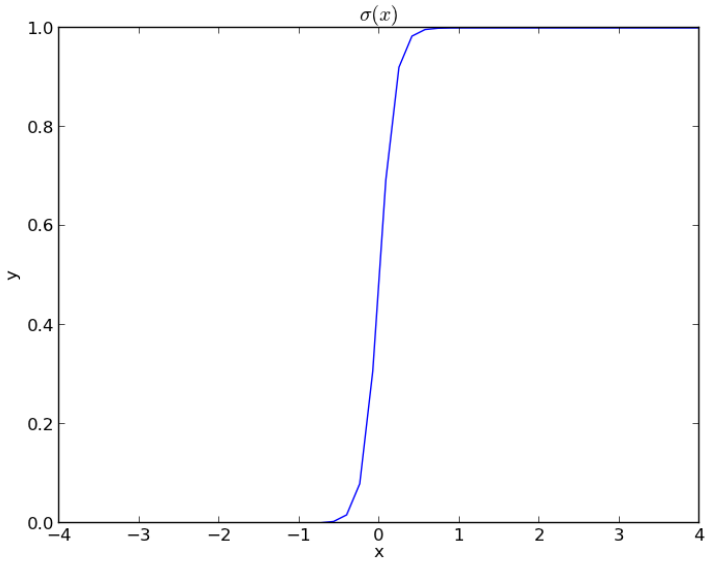


You can see the discontinuity at Re = 3000. What we need is a method to join these two functions smoothly. We can do that with a sigmoid function. Sigmoid functions

A sigmoid function smoothly varies from 0 to 1 according to the equation: $\sigma(x) = \frac{1}{1+e^{-(x-x0)/\alpha}}$. The transition is centered on $x0$, and α determines the width of the transition.

```
x = np.linspace(-4,4);
y = 1.0 / (1 + np.exp(-x / 0.1))
plt.figure(2); plt.clf()
plt.plot(x, y)
plt.xlabel('x'); plt.ylabel('y'); plt.title('$\sigma(x)$')
plt.savefig('images/smooth-transitions-sigma.png')
```

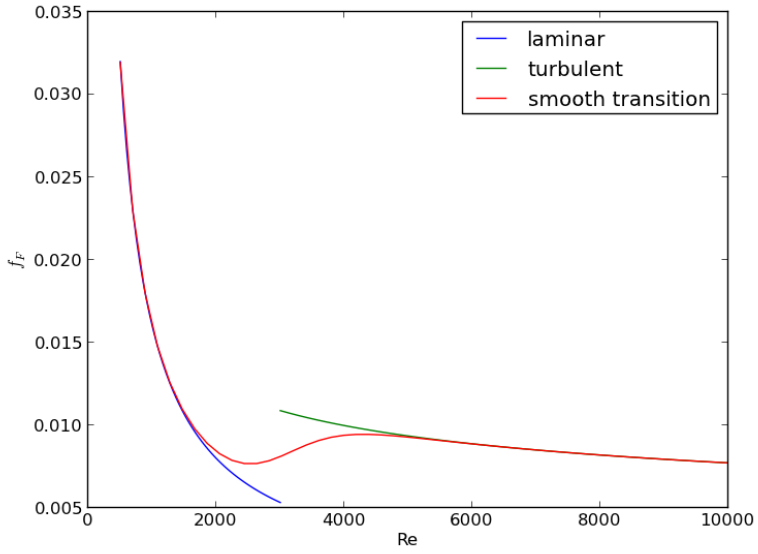
```
>>> <matplotlib.figure.Figure object at 0x0596CF10>
[<matplotlib.lines.Line2D object at 0x05A26D90>]
<matplotlib.text.Text object at 0x059A6050>
<matplotlib.text.Text object at 0x059AF0D0>
<matplotlib.text.Text object at 0x059BEA30>
```



If we have two functions, $f_1(x)$ and $f_2(x)$ we want to smoothly join, we do it like this: $f(x) = (1-\sigma(x))f_1(x)+\sigma(x)f_2(x)$. There is no formal justification for this form of joining, it is simply a mathematical convenience to get a numerically smooth function. Other functions besides the sigmoid function could also be used, as long as they smoothly transition from 0 to 1, or from 1 to zero.

```
def fanning_friction_factor(Re):
    '''combined, continuous correlation for the fanning friction factor.
    the alpha parameter is chosen to provide the desired smoothness.
    The transition region is about +- 4*alpha. The value 450 was
    selected to reasonably match the shape of the correlation
    function provided by Morrison (see last section of this file)'''
    sigma =  1. / (1 + np.exp(-(Re - 3000.0) / 450.0));
    f = (1-sigma) * fF_laminar(Re) + sigma * fF_turbulent(Re)
    return f

Re = np.linspace(500,10000);
f = fanning_friction_factor(Re);

# add data to figure 1
plt.figure(1)
plt.plot(Re,f, label='smooth transition')
plt.xlabel('Re')
plt.ylabel('$f_F$')
plt.legend()
plt.savefig('images/smooth-transitions-3.png')
```

```
... ... ... ... ... ... ... ... >>> >>> >>> >>> ... <matplotlib.figure.Figure object at 0x0
[<matplotlib.lines.Line2D object at 0x05786310>]
<matplotlib.text.Text object at 0x0577CFF0>
<matplotlib.text.Text object at 0x05798790>
<matplotlib.legend.Legend object at 0x05A302B0>
```

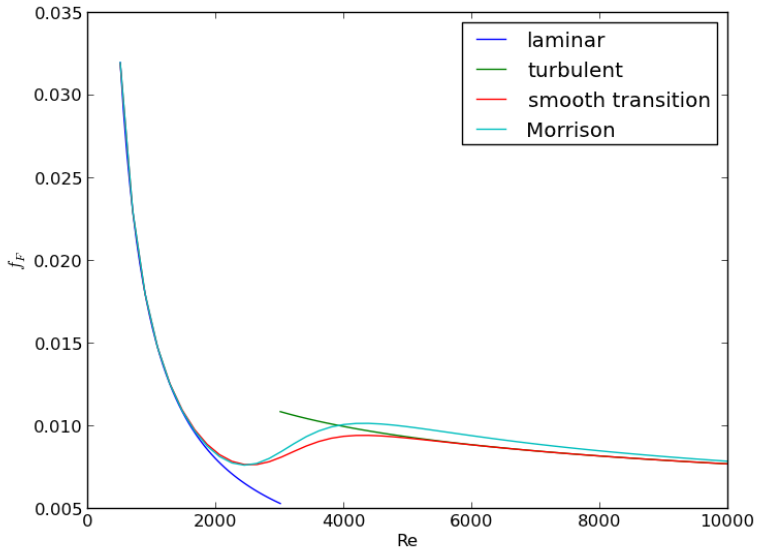


You can see that away from the transition the combined function is practically equivalent to the original two functions. That is because away from the transition the sigmoid function is 0 or 1. Near Re = 3000 is a smooth transition from one curve to the other curve.

Morrison derived a single function for the friction factor correlation over all Re: $f = \frac{0.0076\left(\frac{3170}{Re}\right)^{0.165}}{1+\left(\frac{3171}{Re}\right)^{7.0}} + \frac{16}{Re}$. Here we show the comparison with the approach used above. The friction factor differs slightly at high Re, because Morrison's is based on the Prandlt correlation, while the work here is based on the Nikuradse correlation. They are similar, but not the same.

```
# add this correlation to figure 1
h, = plt.plot(Re, 16.0/Re + (0.0076 * (3170 / Re)**0.165) / (1 + (3170.0 / Re)**7))

ax = plt.gca()
handles, labels = ax.get_legend_handles_labels()

handles.append(h)
labels.append('Morrison')
ax.legend(handles, labels)
plt.savefig('images/smooth-transitions-morrison.png')
```

```
>>> >>> >>> >>> >>> >>> >>> <matplotlib.legend.Legend object at 0x05A5AEB0>
```



3.9.1 Summary

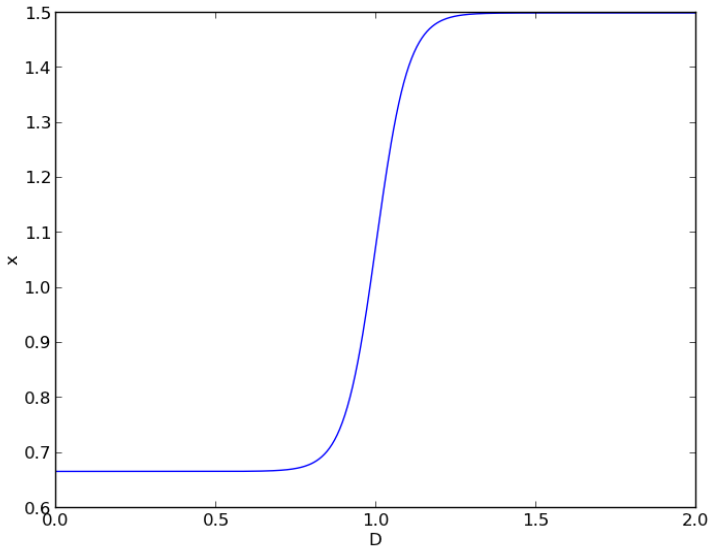
The approach demonstrated here allows one to smoothly join two discontinuous functions that describe physics in different regimes, and that must transition over some range of data. It should be emphasized that the method has no physical basis, it simply allows one to create a mathematically smooth function, which could be necessary for some optimizers or solvers to work.

3.10 Smooth transitions between two constants

Suppose we have a parameter that has two different values depending on the value of a dimensionless number. For example when the dimensionless number is much less than 1, x = 2/3, and when x is much greater than 1, x = 1. We desire a smooth transition from 2/3 to 1 as a function of x to avoid discontinuities in functions of x. We will adapt the smooth transitions between functions to be a smooth transition between constants.

We define our function as $x(D) = x0 + (x1 - x0) * (1 - sigma(D, w)$. We control the rate of the transition by the variable w

```
import numpy as np
import matplotlib.pyplot as plt

x0 = 2.0 / 3.0
x1 = 1.5

w = 0.05

D = np.linspace(0,2, 500)

sigmaD = 1.0 / (1.0 + np.exp(-(1 - D) / w))

x =  x0 + (x1 - x0)*(1 - sigmaD)

plt.plot(D, x)
plt.xlabel('D'); plt.ylabel('x')
plt.savefig('images/smooth-transitions-constants.png')
```



This is a nice trick to get an analytical function with continuous derivatives for a transition between two constants. You could have the transition occur at

a value other than D = 1, as well by changing the argument to the exponential function.

3.11 On the quad or trapz'd in ChemE heaven

Matlab post

What is the difference between quad and trapz? The short answer is that quad integrates functions (via a function handle) using numerical quadrature, and trapz performs integration of arrays of data using the trapezoid method.

Let us look at some examples. We consider the example of computing $\int_0^2 x^3 dx$. the analytical integral is $1/4x^4$, so we know the integral evaluates to $16/4 = 4$. This will be our benchmark for comparison to the numerical methods.

We use the scipy.integrate.quad command to evaluate this $\int_0^2 x^3 dx$.

```
from scipy.integrate import quad

ans, err = quad(lambda x: x**3, 0, 2)
print ans
```

```
4.0
```

you can also define a function for the integrand.

```
from scipy.integrate import quad

def integrand(x):
    return x**3

ans, err = quad(integrand, 0, 2)
print ans
```

```
4.0
```

3.11.1 Numerical data integration

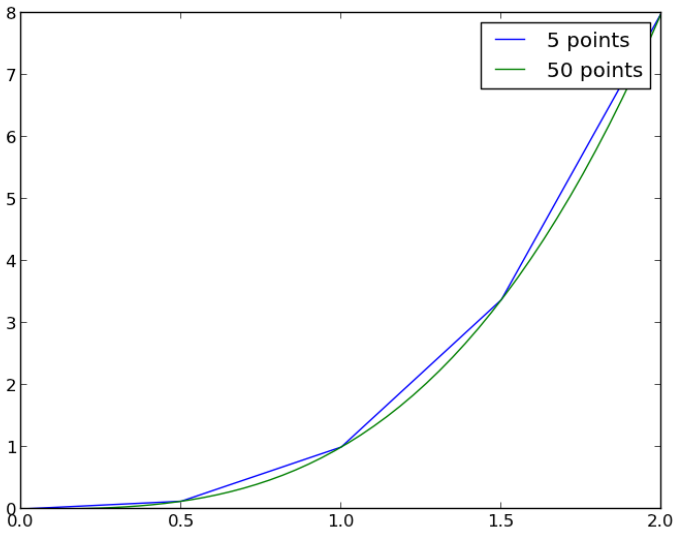
if we had numerical data like this, we use trapz to integrate it

```
import numpy as np

x = np.array([0, 0.5, 1, 1.5, 2])
y = x**3

i2 = np.trapz(y, x)

error = (i2 - 4)/4

print i2, error
```

```
4.25 0.0625
```

Note the integral of these vectors is greater than 4! You can see why here.

```
import numpy as np
import matplotlib.pyplot as plt
x = np.array([0, 0.5, 1, 1.5, 2])
y = x**3

x2 = np.linspace(0, 2)
y2 = x2**3

plt.plot(x, y, label='5 points')
plt.plot(x2, y2, label='50 points')
plt.legend()
plt.savefig('images/quad-1.png')
```



The trapezoid method is overestimating the area significantly. With more points, we get much closer to the analytical value.

```
import numpy as np

x2 = np.linspace(0, 2, 100)
y2 = x2**3

print np.trapz(y2, x2)
```

```
4.00040812162
```

3.11.2 Combining numerical data with quad

You might want to combine numerical data with the quad function if you want to perform integrals easily. Let us say you are given this data:

x = [0 0.5 1 1.5 2]; y = [0 0.1250 1.0000 3.3750 8.0000];

and you want to integrate this from x = 0.25 to 1.75. We do not have data in those regions, so some interpolation is going to be needed. Here is one approach.

```
from scipy.interpolate import interp1d
from scipy.integrate import quad
import numpy as np

x = [0, 0.5, 1, 1.5, 2]
y = [0,    0.1250,    1.0000,    3.3750,    8.0000]

f = interp1d(x, y)

# numerical trapezoid method
xfine = np.linspace(0.25, 1.75)
yfine = f(xfine)
print np.trapz(yfine, xfine)

# quadrature with interpolation
ans, err = quad(f, 0.25, 1.75)
print ans
```

```
2.53199187838
2.53125
```

These approaches are very similar, and both rely on linear interpolation. The second approach is simpler, and uses fewer lines of code.

3.11.3 Summary

trapz and quad are functions for getting integrals. Both can be used with numerical data if interpolation is used. The syntax for the quad and trapz function is different in scipy than in Matlab.

Finally, see this post for an example of solving an integral equation using quad and fsolve.

3.12 Polynomials in python

Matlab post

Polynomials can be represented as a list of coefficients. For example, the polynomial $4 * x^3 + 3 * x^2 - 2 * x + 10 = 0$ can be represented as [4, 3, -2, 10]. Here are some ways to create a polynomial object, and evaluate it.

```
import numpy as np

ppar = [4, 3, -2, 10]
p = np.poly1d(ppar)

print p(3)
print np.polyval(ppar, 3)

x = 3
print 4*x**3 + 3*x**2 -2*x + 10
```

```
139
139
139
```

numpy makes it easy to get the derivative and integral of a polynomial.

Consider: $y = 2x^2 - 1$. We know the derivative is $4x$. Here we compute the derivative and evaluate it at x=4.

```
1  import numpy as np
2
3  p = np.poly1d([2, 0, -1])
4  p2 = np.polyder(p)
5  print p2
6  print p2(4)
```

```
4 x
16
```

The integral of the previous polynomial is $\frac{2}{3}x^3 - x + c$. We assume $C = 0$. Let us compute the integral $\int_2^4 2x^2 - 1dx$.

```
1  import numpy as np
2
3  p = np.poly1d([2, 0, -1])
4  p2 = np.polyint(p)
5  print p2
6  print p2(4) - p2(2)
```

```
        3
0.6667 x - 1 x
35.3333333333
```

One reason to use polynomials is the ease of finding all of the roots using numpy.roots.

```
1  import numpy as np
2  print np.roots([2, 0, -1]) # roots are +- sqrt(2)
3
4  # note that imaginary roots exist, e.g. x^2 + 1 = 0 has two roots, +-i
5  p = np.poly1d([1, 0, 1])
6  print np.roots(p)
```

```
[ 0.70710678 -0.70710678]
[ 0.+1.j  0.-1.j]
```

There are applications of polynomials in thermodynamics. The van der waal equation is a cubic polynomial $f(V) = V^3 - \frac{pnb+nRT}{p}V^2 + \frac{n^2a}{p}V - \frac{n^3ab}{p} = 0$, where a and b are constants, p is the pressure, R is the gas constant, T is an absolute temperature and n is the number of moles. The roots of this equation tell you the volume of the gas at those conditions.

```
import numpy as np
# numerical values of the constants
a = 3.49e4
b = 1.45
p = 679.7   # pressure in psi
T = 683     # T in Rankine
n = 1.136   # lb-moles
R = 10.73       # ft^3 * psi /R / lb-mol

ppar = [1.0, -(p*n*b+n*R*T)/p, n**2*a/p,  -n**3*a*b/p];
print np.roots(ppar)
```

```
[ 5.09432376+0.j          4.40066810+1.43502848j  4.40066810-1.43502848j]
```

Note that only one root is real (and even then, we have to interpet 0.j as not being imaginary. Also, in a cubic polynomial, there can only be two imaginary roots). In this case that means there is only one phase present.

3.12.1 Summary

Polynomials in numpy are even better than in Matlab, because you get a polynomial object that acts just like a function. Otherwise, they are functionally equivalent.

3.13 The trapezoidal method of integration

Matlab post See http://en.wikipedia.org/wiki/Trapezoidal_rule

$$\int_a^b f(x)dx \approx \frac{1}{2}\sum_{k=1}^{N}(x_{k+1} - x_k)(f(x_{k+1}) + f(x_k))$$

Let us compute the integral of sin(x) from x=0 to π. To approximate the integral, we need to divide the interval from a to b into N intervals. The analytical answer is 2.0.

We will use this example to illustrate the difference in performance between loops and vectorized operations in python.

```
import numpy as np
import time

a = 0.0; b = np.pi;
N = 1000; # this is the number of intervals

h = (b - a)/N; # this is the width of each interval
x = np.linspace(a, b, N)
y = np.sin(x); # the sin function is already vectorized

t0 = time.time()
f = 0.0
for k in range(len(x) - 1):
    f += 0.5 * ((x[k+1] - x[k]) * (y[k+1] + y[k]))

tf = time.time() - t0
print 'time elapsed = {0} sec'.format(tf)
```

```

print f
```

```
>>> >>> >>> >>> >>> >>> >>> >>> >>> >>> >>> ... ... >>> >>> time elapsed = 0.0780000686646
>>> 1.99999835177
```

```
t0 = time.time()
Xk = x[1:-1] - x[0:-2] # vectorized version of (x[k+1] - x[k])
Yk = y[1:-1] + y[0:-2] # vectorized version of (y[k+1] + y[k])

f = 0.5 * np.sum(Xk * Yk) # vectorized version of the loop above
tf = time.time() - t0
print 'time elapsed = {0} sec'.format(tf)

print f
```

```
>>> >>> >>> >>> >>> time elapsed = 0.077999830246 sec
>>> 1.99999340709
```

In the last example, there may be loop buried in the sum command. Let us do one final method, using linear algebra, in a single line. The key to understanding this is to recognize the sum is just the result of a dot product of the x differences and y sums.

```
t0 = time.time()
f = 0.5 * np.dot(Xk, Yk)
tf = time.time() - t0
print 'time elapsed = {0} sec'.format(tf)

print f
```

```
>>> >>> time elapsed = 0.0310001373291 sec
>>> 1.99999340709
```

The loop method is straightforward to code, and looks alot like the formula that defines the trapezoid method. the vectorized methods are not as easy to read, and take fewer lines of code to write. However, the vectorized methods are much faster than the loop, so the loss of readability could be worth it for very large problems.

The times here are considerably slower than in Matlab. I am not sure if that is a totally fair comparison. Here I am running python through emacs, which may result in slower performance. I also used a very crude way of timing the performance which lumps some system performance in too.

3.14 simpsons rule

http://docs.scipy.org/doc/scipy/reference/generated/scipy.integrate.simps.html

3.15 Integrating functions in python

Matlab post

Problem statement

find the integral of a function f(x) from a to b i.e.

$$\int_a^b f(x)dx$$

In python we use numerical quadrature to achieve this with the scipy.integrate.quad command.

as a specific example, lets integrate

$$y = x^2$$

from x=0 to x=1. You should be able to work out that the answer is 1/3.

```
from scipy.integrate import quad

def integrand(x):
    return x**2

ans, err = quad(integrand, 0, 1)
print ans
```

```
0.333333333333
```

3.15.1 double integrals

we use the scipy.integrate.dblquad command

Integrate $f(x, y) = ysin(x) + xcos(y)$ over

$\pi <= x <= 2\pi$

$0 <= y <= \pi$

i.e.

$\int_{x=\pi}^{2\pi} \int_{y=0}^{\pi} ysin(x) + xcos(y)dydx$

The syntax in dblquad is a bit more complicated than in Matlab. We have to provide callable functions for the range of the y-variable. Here they are constants, so we create lambda functions that return the constants. Also, note that the order of arguments in the integrand is different than in Matlab.

```
from scipy.integrate import dblquad
import numpy as np

def integrand(y, x):
    'y must be the first argument, and x the second.'
    return y * np.sin(x) + x * np.cos(y)

ans, err = dblquad(integrand, np.pi, 2*np.pi,
                   lambda x: 0,
                   lambda x: np.pi)
print ans
```

```
-9.86960440109
```

we use the tplquad command to integrate $f(x, y, z) = ysin(x) + zcos(x)$ over the region

$0 <= x <= \pi$

$0 <= y <= 1$

$-1 <= z <= 1$

```
from scipy.integrate import tplquad
import numpy as np

def integrand(z, y, x):
    return y * np.sin(x) + z * np.cos(x)

ans, err = tplquad(integrand,
                   0, np.pi,  # x limits
                   lambda x: 0,
                   lambda x: 1, # y limits
                   lambda x,y: -1,
                   lambda x,y: 1) # z limits

print ans
```

```
2.0
```

3.15.2 Summary

scipy.integrate offers the same basic functionality as Matlab does. The syntax differs significantly for these simple examples, but the use of functions for the limits enables freedom to integrate over non-constant limits.

3.16 Integrating equations in python

A common need in engineering calculations is to integrate an equation over some range to determine the total change. For example, say we know the volumetric flow changes with time according to $d\nu/dt = \alpha t$, where $\alpha = 1$ L/min and we want to know how much liquid flows into a tank over 10 minutes if the volumetric flowrate is $\nu_0 = 5$ L/min at $t = 0$. The answer to that question is the value of this integral: $V = \int_0^{10} \nu_0 + \alpha t dt$.

```
import scipy
from scipy.integrate import quad

nu0 = 5     # L/min
alpha = 1.0 # L/min
def integrand(t):
    return nu0 + alpha * t

t0 = 0.0
tfinal = 10.0
V, estimated_error = quad(integrand, t0, tfinal)
print('{0:1.2f} L flowed into the tank over 10 minutes'.format(V))
```

```
100.00 L flowed into the tank over 10 minutes
```

That is all there is too it!

3.17 Romberg integration

http://docs.scipy.org/doc/scipy/reference/generated/scipy.integrate.romberg.html

3.18 http://matlab.cheme.cmu.edu/2011/08/10/symbolic-math-in-matlab/

4 Linear algebra

4.1 Sums products and linear algebra notation - avoiding loops where possible

Matlab comparison

Today we examine some methods of linear algebra that allow us to avoid writing explicit loops in Matlab for some kinds of mathematical operations.

Consider the operation on two vectors **a** and **b**.

$$y = \sum_{i=1}^{n} a_i b_i$$

a = [1 2 3 4 5]
b = [3 6 8 9 10]

4.1.1 Old-fashioned way with a loop

We can compute this with a loop, where you initialize y, and then add the product of the ith elements of a and b to y in each iteration of the loop. This is known to be slow for large vectors

```
a = [1, 2, 3, 4, 5]
b = [3, 6, 8, 9, 10]

sum = 0
for i in range(len(a)):
    sum = sum + a[i] * b[i]
print sum
```

```
125
```

This is an old fashioned style of coding. A more modern, pythonic approach is:

```
a = [1, 2, 3, 4, 5]
b = [3, 6, 8, 9, 10]

sum = 0
for x,y in zip(a,b):
    sum += x * y
print sum
```

```
125
```

4.1.2 The numpy approach

The most compact method is to use the methods in numpy.

```
import numpy as np

a = np.array([1, 2, 3, 4, 5])
b = np.array([3, 6, 8, 9, 10])

print np.sum(a * b)
```

```
125
```

4.1.3 Matrix algebra approach.

The operation defined above is actually a dot product. We an directly compute the dot product in numpy. Note that with 1d arrays, python knows what to do and does not require any transpose operations.

```
import numpy as np

a = np.array([1, 2, 3, 4, 5])
b = np.array([3, 6, 8, 9, 10])

print np.dot(a, b)
```

```
125
```

4.1.4 Another example

Consider $y = \sum_{i=1}^{n} w_i x_i^2$. This operation is like a weighted sum of squares. The old-fashioned way to do this is with a loop.

```
w = [0.1, 0.25, 0.12, 0.45, 0.98];
x = [9, 7, 11, 12, 8];
y = 0
for wi, xi in zip(w,x):
   y += wi * xi**2
print y
```

```
162.39
```

Compare this to the more modern numpy approach.

```
import numpy as np
w = np.array([0.1, 0.25, 0.12, 0.45, 0.98])
x = np.array([9, 7, 11, 12, 8])
y = np.sum(w * x**2)
print y
```

```
162.39
```

We can also express this in matrix algebra form. The operation is equivalent to $y = \vec{x} \cdot D_w \cdot \vec{x}^T$ where D_w is a diagonal matrix with the weights on the diagonal.

```
import numpy as np
w = np.array([0.1, 0.25, 0.12, 0.45, 0.98])
x = np.array([9, 7, 11, 12, 8])
y = np.dot(x, np.dot(np.diag(w), x))
print y
```

```
162.39
```

This last form avoids explicit loops and sums, and relies on fast linear algebra routines.

4.1.5 Last example

Consider the sum of the product of three vectors. Let $y = \sum_{i=1}^{n} w_i x_i y_i$. This is like a weighted sum of products.

```
import numpy as np

w = np.array([0.1, 0.25, 0.12, 0.45, 0.98])
x = np.array([9, 7, 11, 12, 8])
y = np.array([2, 5, 3, 8, 0])

print np.sum(w * x * y)
print np.dot(w, np.dot(np.diag(x), y))
```

```
57.71
57.71
```

4.1.6 Summary

We showed examples of the following equalities between traditional sum notations and linear algebra

$$\mathbf{ab} = \sum_{\mathbf{i=1}}^{\mathbf{n}} \mathbf{a_i b_i}$$

$$\mathbf{x D_w x^T} = \sum_{\mathbf{i=1}}^{\mathbf{n}} \mathbf{w_i x_i^2}$$

$$\mathbf{x D_w y^T} = \sum_{\mathbf{i=1}}^{\mathbf{n}} \mathbf{w_i x_i y_i}$$

These relationships enable one to write the sums as a single line of python code, which utilizes fast linear algebra subroutines, avoids the construction of slow loops, and reduces the opportunity for errors in the code. Admittedly, it introduces the opportunity for new types of errors, like using the wrong relationship, or linear algebra errors due to matrix size mismatches.

4.2 http://matlab.cheme.cmu.edu/2011/08/02/determining-linear-independence-of-a-set-of-vectors/

4.3 Rules for transposition

Matlab comparison

Here are the four rules for matrix multiplication and transposition

1. $(\mathbf{A}^T)^T = \mathbf{A}$
2. $(\mathbf{A} + \mathbf{B})^T = \mathbf{A}^T + \mathbf{B}^T$
3. $(c\mathbf{A})^T = c\mathbf{A}^T$
4. $(\mathbf{AB})^T = \mathbf{B}^T\mathbf{A}^T$

reference: Chapter 7.2 in Advanced Engineering Mathematics, 9th edition. by E. Kreyszig.

4.3.1 The transpose in Python

There are two ways to get the transpose of a matrix: with a notation, and with a function.

```
import numpy as np
A = np.array([[5, -8, 1],
              [4, 0, 0]])

# function
print np.transpose(A)


# notation
print A.T
```

```
 [[ 5  4]
  [-8  0]
  [ 1  0]]
 [[ 5  4]
  [-8  0]
  [ 1  0]]
```

4.3.2 Rule 1

```
import numpy as np

A = np.array([[5, -8, 1],
              [4, 0, 0]])

print np.all(A == (A.T).T)
```

```
 True
```

4.3.3 Rule 2

```
import numpy as np
A = np.array([[5, -8, 1],
              [4, 0, 0]])

B = np.array([[3, 4, 5], [1, 2,3]])

print np.all( A.T + B.T == (A + B).T)
```

```
True
```

4.3.4 Rule 3

```
import numpy as np
A = np.array([[5, -8, 1],
              [4, 0, 0]])

c = 2.1

print np.all( (c*A).T == c*A.T)
```

```
True
```

4.3.5 Rule 4

```
import numpy as np
A = np.array([[5, -8, 1],
              [4, 0, 0]])

B = np.array([[0, 2],
              [1, 2],
              [6, 7]])

print np.all(np.dot(A, B).T == np.dot(B.T, A.T))
```

```
True
```

4.3.6 Summary

That wraps up showing numerically the transpose rules work for these examples.

4.4 Solving linear equations

Given these equations, find [x1, x2, x3]

$$x_1 - x_2 + x_3 = 0 \quad (5)$$
$$10x_2 + 25x_3 = 90 \quad (6)$$
$$20x_1 + 10x_2 = 80 \quad (7)$$

reference: Kreysig, Advanced Engineering Mathematics, 9th ed. Sec. 7.3

When solving linear equations, we can represent them in matrix form. The we simply use `numpy.linalg.solve` to get the solution.

```
import numpy as np
A = np.array([[1, -1, 1],
              [0, 10, 25],
              [20, 10, 0]])

b = np.array([0, 90, 80])

x = np.linalg.solve(A, b)
print x
print np.dot(A,x)

# Let us confirm the solution.
# this shows one element is not equal because of float tolerance
print np.dot(A,x) == b

# here we use a tolerance comparison to show the differences is less
# than a defined tolerance.
TOLERANCE = 1e-12
print np.abs((np.dot(A, x) - b)) <= TOLERANCE
```

```
[ 2.  4.  2.]
[  2.66453526e-15   9.00000000e+01   8.00000000e+01]
[False  True  True]
[ True  True  True]
```

It can be useful to confirm there should be a solution, e.g. that the equations are all independent. The matrix rank will tell us that. Note that numpy:rank does not give you the matrix rank, but rather the number of dimensions of the array. We compute the rank by computing the number of singular values of the matrix that are greater than zero, within a prescribed tolerance. We use the `numpy.linalg.svd` function for that. In Matlab you would use the rref command to see if there are any rows that are all zero, but this command does not exist in numpy. That command does not have practical use in numerical linear algebra and has not been implemented.

```
import numpy as np
A = np.array([[1, -1, 1],
              [0, 10, 25],
              [20, 10, 0]])

b = np.array([0, 90, 80])

# determine number of independent rows in A we get the singular values
# and count the number greater than 0.
TOLERANCE = 1e-12
u, s, v = np.linalg.svd(A)
print 'Singular values: {0}'.format(s)
print '# of independent rows: {0}'.format(np.sum(np.abs(s) > TOLERANCE))

# to illustrate a case where there are only 2 independent rows
# consider this case where row3 = 2*row2.
A = np.array([[1, -1, 1],
              [0, 10, 25],
              [0, 20, 50]])

u, s, v = np.linalg.svd(A)

print 'Singular values: {0}'.format(s)
print '# of independent rows: {0}'.format(np.sum(np.abs(s) > TOLERANCE))
```

```
Singular values: [ 27.63016717  21.49453733   1.5996022 ]
# of independent rows: 3
Singular values: [ 60.21055203   1.63994657  -0.        ]
# of independent rows: 2
```

Matlab comparison

5 Nonlinear algebra

5.1 Solving integral equations with fsolve

Original post in Matlab

Occasionally we have integral equations we need to solve in engineering problems, for example, the volume of plug flow reactor can be defined by this equation: $V = \int_{Fa(V=0)}^{Fa} \frac{1}{r_a} dFa$ where r_a is the rate law. Suppose we know the reactor volume is 100 L, the inlet molar flow of A is 1 mol/L, the volumetric flow is 10 L/min, and $r_a = -kCa$, with $k = 0.23$ 1/min. What is the exit molar flow rate? We need to solve the following equation:

$$100 = \int_{Fa(V=0)}^{Fa} \frac{1}{-kFa/\nu} dFa$$

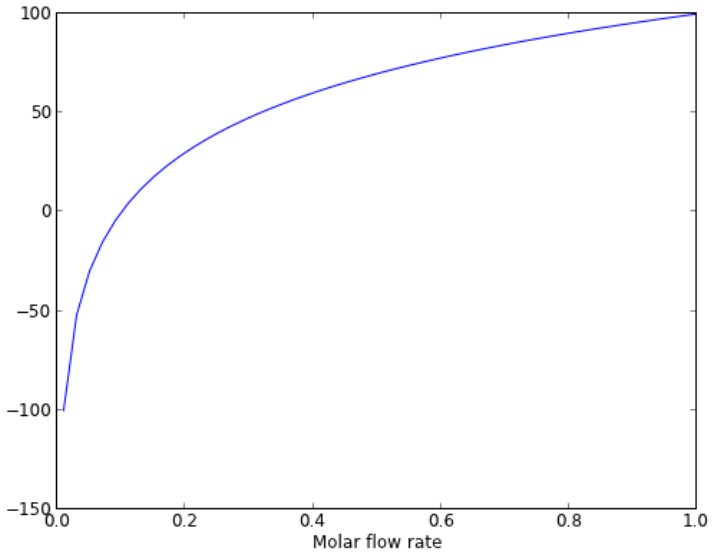
We start by creating a function handle that describes the integrand. We can use this function in the quad command to evaluate the integral.

```
1  import numpy as np
2  from scipy.integrate import quad
3  from scipy.optimize import fsolve
4
5  k = 0.23
6  nu = 10.0
7  Fao = 1.0
8
9  def integrand(Fa):
10     return -1.0 / (k * Fa / nu)
11
12 def func(Fa):
13     integral,err = quad(integrand, Fao, Fa)
14     return 100.0 - integral
15
16 vfunc = np.vectorize(func)
```

We will need an initial guess, so we make a plot of our function to get an idea.

```
1  import matplotlib.pyplot as plt
2
3  f = np.linspace(0.01, 1)
4  plt.plot(f, vfunc(f))
5  plt.xlabel('Molar flow rate')
6  plt.savefig('images/integral-eqn-guess.png')
7  plt.show()
```

```
>>> >>> [<matplotlib.lines.Line2D object at 0x964a910>]
<matplotlib.text.Text object at 0x961fe50>
```



Now we can see a zero is near Fa = 0.1, so we proceed to solve the equation.

```
Fa_guess = 0.1
Fa_exit, = fsolve(vfunc, Fa_guess)
print 'The exit concentration is {0:1.2f} mol/L'.format(Fa_exit / nu)
```

```
>>> The exit concentration is 0.01 mol/L
```

5.1.1 Summary notes

This example seemed a little easier in Matlab, where the quad function seemed to get automatically vectorized. Here we had to do it by hand.

5.2 Method of continuity for nonlinear equation solving

Matlab post Adapted from Perry's Chemical Engineers Handbook, 6th edition 2-63.

We seek the solution to the following nonlinear equations:

$2 + x + y - x^2 + 8xy + y^3 = 0$

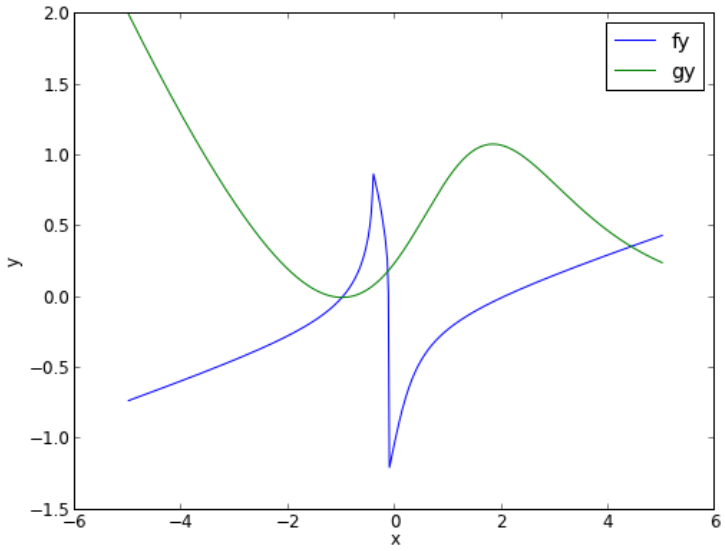
$1 + 2x - 3y + x^2 + xy - ye^x = 0$

In principle this is easy, we simply need some initial guesses and a nonlinear solver. The challenge here is what would you guess? There could be many

solutions. The equations are implicit, so it is not easy to graph them, but let us give it a shot, starting on the x range -5 to 5. The idea is set a value for x, and then solve for y in each equation.

```
import numpy as np
from scipy.optimize import fsolve

import matplotlib.pyplot as plt

def f(x, y):
    return 2 + x + y - x**2 + 8*x*y + y**3;

def g(x, y):
    return 1 + 2*x - 3*y + x**2 + x*y - y*np.exp(x)

x = np.linspace(-5, 5, 500)

@np.vectorize
def fy(x):
    x0 = 0.0
    def tmp(y):
        return f(x, y)
    y1, = fsolve(tmp, x0)
    return y1

@np.vectorize
def gy(x):
    x0 = 0.0
    def tmp(y):
        return g(x, y)
    y1, = fsolve(tmp, x0)
    return y1


plt.plot(x, fy(x), x, gy(x))
plt.xlabel('x')
plt.ylabel('y')
plt.legend(['fy', 'gy'])
plt.savefig('images/continuation-1.png')
```

```
>>> >>> >>> >>> ... ... >>> ... ... >>> >>> >>> ... ... ... ... ... ... ... >>> ... ... ...
  improvement from the last ten iterations.
  warnings.warn(msg, RuntimeWarning)
/opt/kitchingroup/enthought/epd-7.3-2-rh5-x86_64/lib/python2.7/site-packages/scipy/optimize/
  improvement from the last five Jacobian evaluations.
  warnings.warn(msg, RuntimeWarning)
[<matplotlib.lines.Line2D object at 0x1a0c4990>, <matplotlib.lines.Line2D object at 0x1a0c4a
<matplotlib.text.Text object at 0x19d5e390>
<matplotlib.text.Text object at 0x19d61d90>
<matplotlib.legend.Legend object at 0x189df850>
```



You can see there is a solution near x = -1, y = 0, because both functions equal zero there. We can even use that guess with fsolve. It is disappointly easy! But, keep in mind that in 3 or more dimensions, you cannot perform this visualization, and another method could be required.

```
1  def func(X):
2      x,y = X
3      return [f(x, y), g(x, y)]
4
5  print fsolve(func, [-2, -2])
```

```
... ... >>> [ -1.00000000e+00   1.28730858e-15]
```

We explore a method that bypasses this problem today. The principle is to introduce a new variable, λ, which will vary from 0 to 1. at $\lambda = 0$ we will have a simpler equation, preferrably a linear one, which can be easily solved, or which can be analytically solved. At $\lambda = 1$, we have the original equations. Then, we create a system of differential equations that start at the easy solution, and integrate from $\lambda = 0$ to $\lambda = 1$, to recover the final solution.

We rewrite the equations as:

$f(x, y) = (2 + x + y) + \lambda(-x^2 + 8xy + y^3) = 0$

$g(x, y) = (1 + 2x - 3y) + \lambda(x^2 + xy - ye^x) = 0$

Now, at $\lambda = 0$ we have the simple linear equations:

$x + y = -2$

$2x - 3y = -1$

These equations are trivial to solve:

```
x0 = np.linalg.solve([[1., 1.], [2., -3.]],[ -2, -1])
print x0
```

```
[-1.4 -0.6]
```

We form the system of ODEs by differentiating the new equations with respect to λ. Why do we do that? The solution, (x,y) will be a function of λ. From calculus, you can show that:

$\frac{\partial f}{\partial x}\frac{\partial x}{\partial \lambda} + \frac{\partial f}{\partial y}\frac{\partial y}{\partial \lambda} = -\frac{\partial f}{\partial \lambda}$
$\frac{\partial g}{\partial x}\frac{\partial x}{\partial \lambda} + \frac{\partial g}{\partial y}\frac{\partial y}{\partial \lambda} = -\frac{\partial g}{\partial \lambda}$

Now, solve this for $\frac{\partial x}{\partial \lambda}$ and $\frac{\partial y}{\partial \lambda}$. You can use Cramer's rule to solve for these to yield:

$$\frac{\partial x}{\partial \lambda} = \frac{\partial f/\partial y \partial g/\partial \lambda - \partial f/\partial \lambda \partial g/\partial y}{\partial f/\partial x \partial g/\partial y - \partial f/\partial y \partial g/\partial x} \tag{8}$$

$$\tag{9}$$

$$\frac{\partial y}{\partial \lambda} = \frac{\partial f/\partial \lambda \partial g/\partial x - \partial f/\partial x \partial g/\partial \lambda}{\partial f/\partial x \partial g/\partial y - \partial f/\partial y \partial g/\partial x} \tag{10}$$

For this set of equations:

$$\partial f/\partial x = 1 - 2\lambda x + 8\lambda y \tag{11}$$

$$\tag{12}$$

$$\partial f/\partial y = 1 + 8\lambda x + 3\lambda y^2 \tag{13}$$

$$\tag{14}$$

$$\partial g/\partial x = 2 + 2\lambda x + \lambda y - \lambda y e^x \tag{15}$$

$$\tag{16}$$

$$\partial g/\partial y = -3 + \lambda x - \lambda e^x \tag{17}$$

Now, we simply set up those two differential equations on $\frac{\partial x}{\partial \lambda}$ and $\frac{\partial y}{\partial \lambda}$, with the initial conditions at $\lambda = 0$ which is the solution of the simpler linear equations, and integrate to $\lambda = 1$, which is the final solution of the original equations!

```
def ode(X, LAMBDA):
    x,y = X
    pfpx = 1.0 - 2.0 * LAMBDA * x + 8 * LAMBDA * y
    pfpy = 1.0 + 8.0 * LAMBDA * x + 3.0 * LAMBDA * y**2
    pfpLAMBDA = -x**2 + 8.0 * x * y + y**3;
    pgpx = 2. + 2. * LAMBDA * x + LAMBDA * y - LAMBDA * y * np.exp(x)
    pgpy = -3. + LAMBDA * x - LAMBDA * np.exp(x)
    pgpLAMBDA = x**2 + x * y - y * np.exp(x);
    dxdLAMBDA = (pfpy * pgpLAMBDA - pfpLAMBDA * pgpy) / (pfpx * pgpy - pfpy * pgpx)
    dydLAMBDA = (pfpLAMBDA * pgpx - pfpx * pgpLAMBDA) / (pfpx * pgpy - pfpy * pgpx)
    dXdLAMBDA = [dxdLAMBDA, dydLAMBDA]
    return dXdLAMBDA
```

```
13
14
15  from scipy.integrate import odeint
16
17  lambda_span = np.linspace(0, 1, 100)
18
19  X = odeint(ode, x0, lambda_span)
20
21  xsol, ysol = X[-1]
22  print 'The solution is at x={0:1.3f}, y={1:1.3f}'.format(xsol, ysol)
23  print f(xsol, ysol), g(xsol, ysol)
```

```
... ... ... ... ... ... ... ... ... >>> >>> >>> >>> >>> >>> >>> The solution is at x=-1.000
-1.27746598808e-06 -1.15873819107e-06
```

You can see the solution is somewhat approximate; the true solution is x = -1, y = 0. The approximation could be improved by lowering the tolerance on the ODE solver. The functions evaluate to a small number, close to zero. You have to apply some judgment to determine if that is sufficiently accurate. For instance if the units on that answer are kilometers, but you need an answer accurate to a millimeter, this may not be accurate enough.

This is a fair amount of work to get a solution! The idea is to solve a simple problem, and then gradually turn on the hard part by the lambda parameter. What happens if there are multiple solutions? The answer you finally get will depend on your $\lambda = 0$ starting point, so it is possible to miss solutions this way. For problems with lots of variables, this would be a good approach if you can identify the easy problem.

5.3 http://matlab.cheme.cmu.edu/2011/11/02/method-of-continuity-for-solving-nonlinear-equations-part-ii-2/

5.4 Counting roots

Matlab post The goal here is to determine how many roots there are in a nonlinear function we are interested in solving. For this example, we use a cubic polynomial because we know there are three roots.

$$f(x) = x^3 + 6x^2 - 4x - 24$$

5.4.1 Use roots for this polynomial

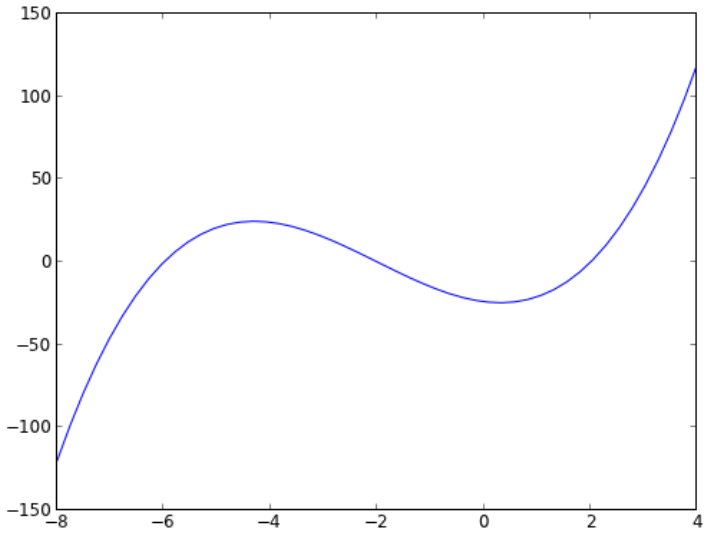
This ony works for a polynomial, it does not work for any other nonlinear function.

```
1  import numpy as np
2  print np.roots([1, 6, -4, -24])
```

```
[-6.  2. -2.]
```

Let us plot the function to see where the roots are.

```
import numpy as np
import matplotlib.pyplot as plt

x = np.linspace(-8, 4)
y = x**3 + 6 * x**2 - 4*x - 24
plt.plot(x, y)
plt.savefig('images/count-roots-1.png')
```



Now we consider several approaches to counting the number of roots in this interval. Visually it is pretty easy, you just look for where the function crosses zero. Computationally, it is tricker.

5.4.2 method 1

Count the number of times the sign changes in the interval. What we have to do is multiply neighboring elements together, and look for negative values. That indicates a sign change. For example the product of two positive or negative numbers is a positive number. You only get a negative number from the product of a positive and negative number, which means the sign changed.

```
import numpy as np
import matplotlib.pyplot as plt

x = np.linspace(-8, 4)
y = x**3 + 6 * x**2 - 4*x - 24

print np.sum(y[0:-2] * y[1:-1] < 0)
```

3

This method gives us the number of roots, but not where the roots are.

5.4.3 Method 2

Using events in an ODE solver python can identify events in the solution to an ODE, for example, when a function has a certain value, e.g. f(x) = 0. We can take advantage of this to find the roots and number of roots in this case. We take the derivative of our function, and integrate it from an initial starting point, and define an event function that counts zeros.

$$f'(x) = 3x^2 + 12x - 4$$

with f(-8) = -120

```
import numpy as np
from pycse import odelay

def fprime(f, x):
    return 3.0 * x**2 + 12.0*x - 4.0

def event(f, x):
    value = f # we want f = 0
    isterminal = False
    direction = 0
    return value, isterminal, direction

xspan = np.linspace(-8, 4)
f0 = -120

X, F, TE, YE, IE = odelay(fprime, f0, xspan, events=[event])
for te, ye in zip(TE, YE):
    print 'root found at x = {0: 1.3f}, f={1: 1.3f}'.format(te, ye)
```

```
root found at x = -6.000, f=-0.000
root found at x = -2.000, f=-0.000
root found at x =  2.000, f= 0.000
```

5.5 http://matlab.cheme.cmu.edu/2011/09/02/know-your-tolerance/

6 Differential equations

6.1 Ordinary differential equations

6.1.1 Numerical solution to a simple ode

Matlab post

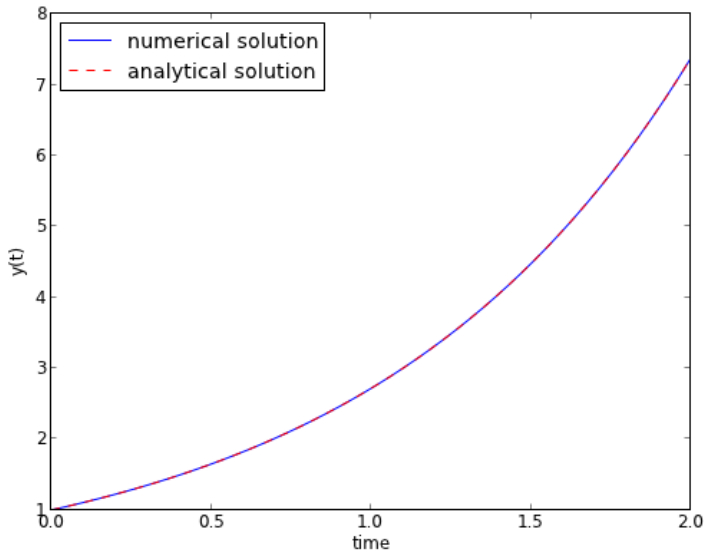
Integrate this ordinary differential equation (ode):

$$\frac{dy}{dt} = y(t)$$

over the time span of 0 to 2. The initial condition is y(0) = 1.

to solve this equation, you need to create a function of the form: dydt = f(y, t) and then use one of the odesolvers, e.g. odeint.

```
import numpy as np
from scipy.integrate import odeint
import matplotlib.pyplot as plt

def fprime(y,t):
    return y

tspan = np.linspace(0, 2)
y0 = 1
ysol = odeint(fprime, y0, tspan)

plt.plot(tspan, ysol, label='numerical solution')
plt.plot(tspan, np.exp(tspan), 'r--', label='analytical solution')
plt.xlabel('time')
plt.ylabel('y(t)')
plt.legend(loc='best')
plt.savefig('images/simple-ode.png')
```



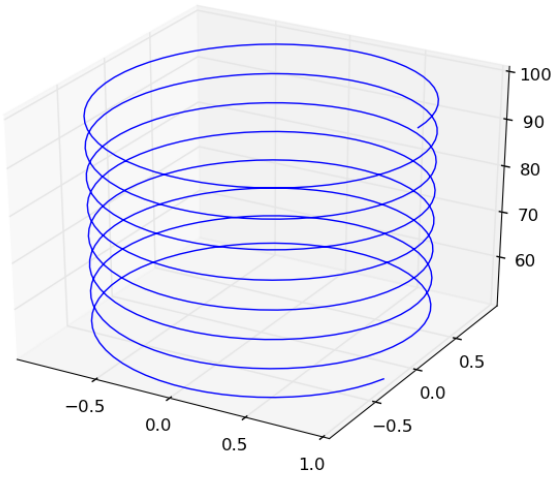
The numerical and analytical solutions agree.

6.1.2 Plotting ODE solutions in cylindrical coordinates

Matlab post

It is straightforward to plot functions in Cartesian coordinates. It is less convenient to plot them in cylindrical coordinates. Here we solve an ODE in cylindrical coordinates, and then convert the solution to Cartesian coordinates for simple plotting.

```
import numpy as np
from scipy.integrate import odeint

def dfdt(F, t):
    rho, theta, z = F
    drhodt = 0   # constant radius
    dthetadt = 1 # constant angular velocity
    dzdt = -1    # constant dropping velocity
    return [drhodt, dthetadt, dzdt]

# initial conditions
rho0 = 1
theta0 = 0
z0 = 100

tspan = np.linspace(0, 50, 500)
sol = odeint(dfdt, [rho0, theta0, z0], tspan)

rho = sol[:,0]
theta = sol[:,1]
z = sol[:,2]

# convert cylindrical coords to cartesian for plotting.
X = rho * np.cos(theta)
Y = rho * np.sin(theta)

from mpl_toolkits.mplot3d import Axes3D
import matplotlib.pyplot as plt
fig = plt.figure()
ax = fig.gca(projection='3d')
ax.plot(X, Y, z)
plt.savefig('images/ode-cylindrical.png')
```



6.1.3 ODEs with discontinuous forcing functions

Matlab post

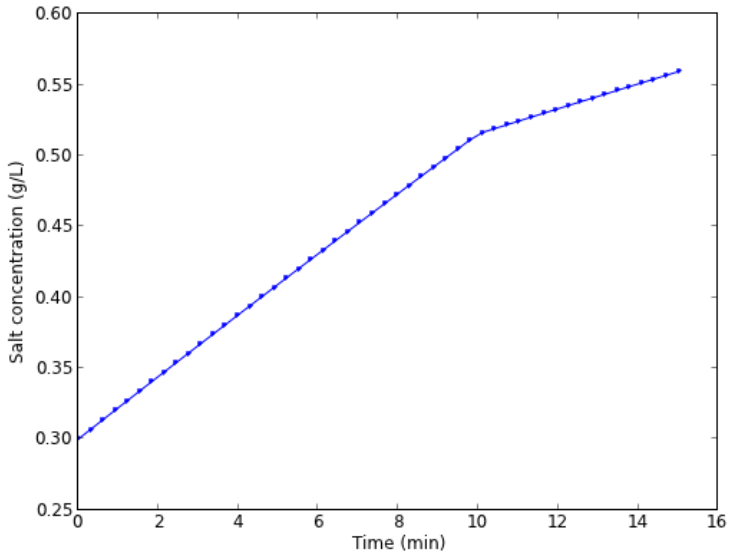
Adapted from http://archives.math.utk.edu/ICTCM/VOL18/S046/paper.pdf

A mixing tank initially contains 300 g of salt mixed into 1000 L of water. At t=0 min, a solution of 4 g/L salt enters the tank at 6 L/min. At t=10 min, the solution is changed to 2 g/L salt, still entering at 6 L/min. The tank is well stirred, and the tank solution leaves at a rate of 6 L/min. Plot the concentration of salt (g/L) in the tank as a function of time.

A mass balance on the salt in the tank leads to this differential equation: $\frac{dM_S}{dt} = \nu C_{S,in}(t) - \nu M_S/V$ with the initial condition that $M_S(t = 0) = 300$. The wrinkle is that the inlet conditions are not constant.

$$C_{S,in}(t) = \begin{array}{ll} 0 & t \leq 0, \\ 4 & 0 < t \leq 10, \\ 2 & t > 10. \end{array}$$

```
import numpy as np
from scipy.integrate import odeint
import matplotlib.pyplot as plt

V = 1000.0 # L
nu = 6.0  # L/min

def Cs_in(t):
    'inlet concentration'
    if t < 0:
        Cs = 0.0 # g/L
    elif (t > 0) and (t <= 10):
        Cs = 4.0
    else:
        Cs = 2.0
    return Cs

def mass_balance(Ms, t):
    '$\frac{dM_S}{dt} = \nu C_{S,in}(t) - \nu M_S/V$'
    dMsdt = nu * Cs_in(t) - nu * Ms / V
    return dMsdt

tspan = np.linspace(0.0, 15.0, 50)

M0 = 300.0 # gm salt
Ms = odeint(mass_balance, M0, tspan)

plt.plot(tspan, Ms/V, 'b.-')
plt.xlabel('Time (min)')
plt.ylabel('Salt concentration (g/L)')
plt.savefig('images/ode-discont.png')
```



You can see the discontinuity in the salt concentration at 10 minutes due to the discontinous change in the entering salt concentration.

6.1.4 Simulating the events feature of Matlab's ode solvers

The ode solvers in Matlab allow you create functions that define events that can stop the integration, detect roots, etc... We will explore how to get a similar effect in python. Here is an example that somewhat does this, but it is only an approximation. We will manually integrate the ODE, adjusting the time step in each iteration to zero in on the solution. When the desired accuracy is reached, we stop the integration.

It does not appear that events are supported in scipy. A solution is at http://mail.scipy.org/pipermail/scipy-dev/2005-July/003078.html, but it does not appear integrated into scipy yet (8 years later ;).

```
1  import numpy as np
2  from scipy.integrate import odeint
3
4  def dCadt(Ca, t):
5      "the ode function"
6      k = 0.23
7      return -k * Ca**2
8
9  Ca0 = 2.3
10
11 # create lists to store time span and solution
12 tspan = [0, ]
13 sol = [Ca0,]
14 i = 0
15
16 while i < 100:   # take max of 100 steps
17     t1 = tspan[i]
```

```
    Ca = sol[i]

    # pick the next time using a Newton-Raphson method
    # we want f(t, Ca) = (Ca(t) - 1)**2 = 0
    # df/dt = df/dCa dCa/dt
    #       = 2*(Ca - 1) * dCadt
    t2 = t1 - (Ca - 1.0)**2 / (2 * (Ca - 1) *dCadt(Ca, t1))

    f = odeint(dCadt, Ca, [t1, t2])

    if np.abs(Ca - 1.0) <= 1e-4:
        print 'Solution reached at i = {0}'.format(i)
        break

    tspan += [t2]
    sol.append(f[-1][0])
    i += 1

print 'At t={0:1.2f}  Ca = {1:1.3f}'.format(tspan[-1], sol[-1])

import matplotlib.pyplot as plt
plt.plot(tspan, sol, 'bo')
plt.show()
```

```
Solution reached at i = 15
At t=2.46  Ca = 1.000
```

This particular solution works for this example, probably because it is well behaved. It is "downhill" to the desired solution. It is not obvious this would work for every example, and it is certainly possible the algorithm could go "backward" in time. A better approach might be to integrate forward until you detect a sign change in your event function, and then refine it in a separate loop.

I like the events integration in Matlab better, but this is actually pretty functional. It should not be too hard to use this for root counting, e.g. by counting sign changes. It would be considerably harder to get the actual roots. It might also be hard to get the positions of events that include the sign or value of the derivatives at the event points.

ODE solving in Matlab is considerably more advanced in functionality than in scipy. There do seem to be some extra packages, e.g. pydstools, scikits.odes that add extra ode functionality.

6.1.5 Mimicking ode events in python

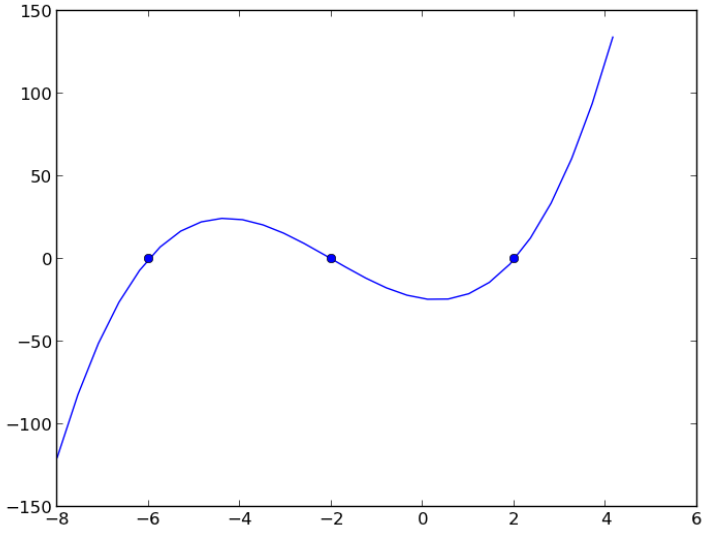
The ODE functions in scipy.integrate do not directly support events like the functions in Matlab do. We can achieve something like it though, by digging into the guts of the solver, and writing a little code. In previous example I used an event to count the number of roots in a function by integrating the derivative of the function.

```
import numpy as np
from scipy.integrate import odeint

def myode(f, x):
    return 3*x**2 + 12*x -4

```

```
7   def event(f, x):
8       'an event is when f = 0'
9       return f
10
11  # initial conditions
12  x0 = -8
13  f0 = -120
14
15  # final x-range and step to integrate over.
16  xf = 4   #final x value
17  deltax = 0.45 #xstep
18
19  # lists to store the results in
20  X = [x0]
21  sol = [f0]
22  e = [event(f0, x0)]
23  events = []
24  x2 = x0
25  # manually integrate at each time step, and check for event sign changes at each step
26  while x2 <= xf: #stop integrating when we get to xf
27      x1 = X[-1]
28      x2 = x1 + deltax
29      f1 = sol[-1]
30
31      f2 = odeint(myode, f1, [x1, x2]) # integrate from x1,f1 to x2,f2
32      X += [x2]
33      sol += [f2[-1][0]]
34
35      # now evaluate the event at the last position
36      e += [event(sol[-1], X[-1])]
37
38      if e[-1] * e[-2] < 0:
39          # Event detected where the sign of the event has changed. The
40          # event is between xPt = X[-2] and xLt = X[-1]. run a modified bisect
41          # function to narrow down to find where event = 0
42          xLt = X[-1]
43          fLt = sol[-1]
44          eLt = e[-1]
45
46          xPt = X[-2]
47          fPt = sol[-2]
48          ePt = e[-2]
49
50          j = 0
51          while j < 100:
52              if np.abs(xLt - xPt) < 1e-6:
53                  # we know the interval to a prescribed precision now.
54                  # print 'Event found between {0} and {1}'.format(x1t, x2t)
55                  print 'x = {0}, event = {1}, f = {2}'.format(xLt, eLt, fLt)
56                  events += [(xLt, fLt)]
57                  break # and return to integrating
58
59              m = (ePt - eLt)/(xPt - xLt) #slope of line connecting points
60                                          #bracketing zero
61
62              #estimated x where the zero is
63              new_x = -ePt / m + xPt
64
65              # now get the new value of the integrated solution at that new x
66              f  = odeint(myode, fPt, [xPt, new_x])
67              new_f = f[-1][-1]
68              new_e = event(new_f, new_x)
69
70              # now check event sign change
71              if eLt * new_e > 0:
72                  xPt = new_x
73                  fPt = new_f
74                  ePt = new_e
```

```
            else:
                xLt = new_x
                fLt = new_f
                eLt = new_e

            j += 1


import matplotlib.pyplot as plt
plt.plot(X, sol)

# add event points to the graph
for x,e in events:
    plt.plot(x,e,'bo ')
plt.savefig('images/event-ode-1.png')
```

```
x = -6.00000006443, event = -4.63518112781e-15, f = -4.63518112781e-15
x = -1.99999996234, event = -1.40512601554e-15, f = -1.40512601554e-15
x = 1.99999988695, event = -1.11022302463e-15, f = -1.11022302463e-15
```

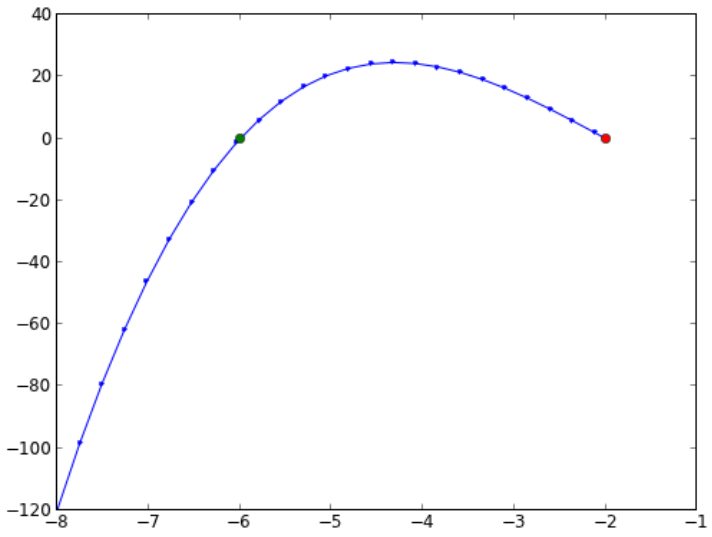


That was a lot of programming to do something like find the roots of the function! Below is an example of using a function coded into pycse to solve the same problem. It is a bit more sophisticated because you can define whether an event is terminal, and the direction of the approach to zero for each event.

```
from pycse import *
import numpy as np

def myode(f, x):
    return 3*x**2 + 12*x -4

def event1(f, x):
    'an event is when f = 0 and event is decreasing'
```

```
    isterminal = True
    direction = -1
    return f, isterminal, direction

def event2(f, x):
    'an event is when f = 0 and increasing'
    isterminal = False
    direction = 1
    return f, isterminal, direction

f0 = -120

xspan = np.linspace(-8, 4)
X, F, TE, YE, IE = odelay(myode, f0, xspan, events=[event1, event2])

import matplotlib.pyplot as plt
plt.plot(X, F, '.-')

# plot the event locations.use a different color for each event
colors = 'rg'

for x,y,i in zip(TE, YE, IE):
    plt.plot([x], [y], 'o', color=colors[i])

plt.savefig('images/event-ode-2.png')
plt.show()
print TE, YE, IE
```

```
[-6.0000001083101306, -1.9999999635550625] [-3.0871138978483259e-14, -7.7715611723760958e-1
```



6.1.6 Solving an ode for a specific solution value

Matlab post The analytical solution to an ODE is a function, which can be solved to get a particular value, e.g. if the solution to an ODE is y(x) = exp(x),

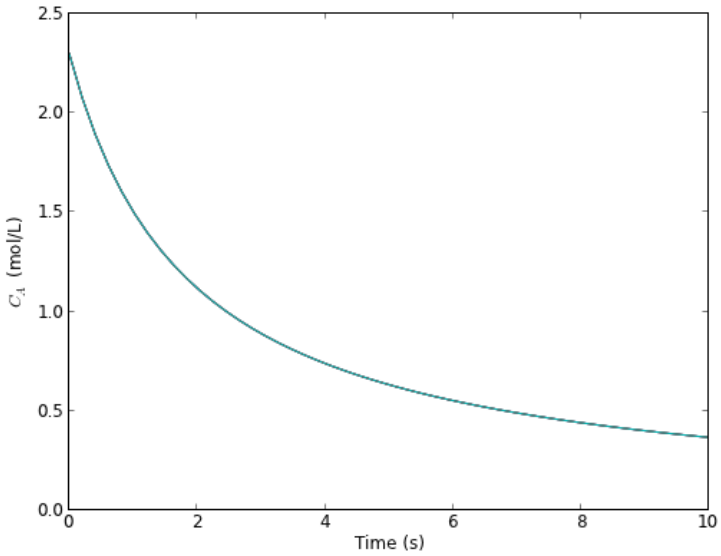
you can solve the solution to find the value of x that makes $y(x) = 2$. In a numerical solution to an ODE we get a vector of independent variable values, and the corresponding function values at those values. To solve for a particular function value we need a different approach. This post will show one way to do that in python.

Given that the concentration of a species A in a constant volume, batch reactor obeys this differential equation $\frac{dC_A}{dt} = -kC_A^2$ with the initial condition $C_A(t = 0) = 2.3$ mol/L and $k = 0.23$ L/mol/s, compute the time it takes for C_A to be reduced to 1 mol/L.

We will get a solution, then create an interpolating function and use fsolve to get the answer.

```
from scipy.integrate import odeint
from scipy.interpolate import interp1d
from scipy.optimize import fsolve
import numpy as np
import matplotlib.pyplot as plt

k = 0.23
Ca0 = 2.3

def dCadt(Ca, t):
    return -k * Ca**2

tspan = np.linspace(0, 10)

sol = odeint(dCadt, Ca0, tspan)
Ca = sol[:,0]

plt.plot(tspan, Ca)
plt.xlabel('Time (s)')
plt.ylabel('$C_A$ (mol/L)')
plt.savefig('images/ode-specific-1.png')
```

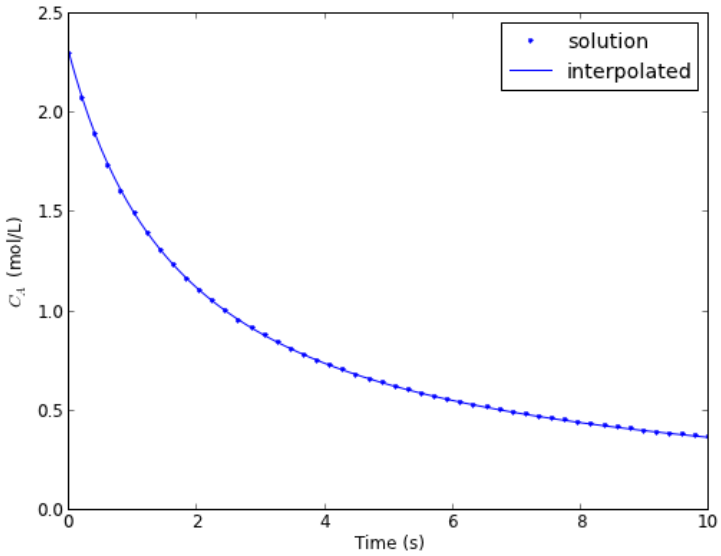
```
>>> >>> >>> >>> ... >>> [<matplotlib.lines.Line2D object at 0x1b710d50>]
<matplotlib.text.Text object at 0x1b2f8410>
<matplotlib.text.Text object at 0x1b2fae10>
```



You can see the solution is near two seconds. Now we create an interpolating function to evaluate the solution. We will plot the interpolating function on a finer grid to make sure it seems reasonable.

```
ca_func = interp1d(tspan, Ca, 'cubic')

itime = np.linspace(0, 10, 200)

plt.figure()
plt.plot(tspan, Ca, '.')
plt.plot(itime, ca_func(itime), 'b-')

plt.xlabel('Time (s)')
plt.ylabel('$C_A$ (mol/L)')
plt.legend(['solution','interpolated'])
plt.savefig('images/ode-specific-2.png')
plt.show()
```

```
>>> >>> >>> <matplotlib.figure.Figure object at 0x1b2dfed0>
[<matplotlib.lines.Line2D object at 0x1c103b90>]
[<matplotlib.lines.Line2D object at 0x1c107050>]
>>> <matplotlib.text.Text object at 0x1c0e65d0>
<matplotlib.text.Text object at 0x1b95bfd0>
<matplotlib.legend.Legend object at 0x1c107550>
```



that loos pretty reasonable. Now we solve the problem.

```
tguess = 2.0
tsol, = fsolve(lambda t: 1.0 - ca_func(t), tguess)
print tsol

# you might prefer an explicit function
def func(t):
    return 1.0 - ca_func(t)

tsol2, = fsolve(func, tguess)
print tsol2
```

```
>>> 2.4574668235
>>> ... ... >>> 2.4574668235
```

That is it. Interpolation can provide a simple way to evaluate the numerical solution of an ODE at other values.

For completeness we examine a final way to construct the function. We can actually integrate the ODE in the function to evaluate the solution at the point of interest. If it is not computationally expensive to evaluate the ODE solution this works fine. Note, however, that the ODE will get integrated from 0 to the value t for each iteration of fsolve.

```
def func(t):
    tspan = [0, t]
    sol = odeint(dCadt, Ca0, tspan)
    return 1.0 - sol[-1]

```

```
tsol3, = fsolve(func, tguess)
print tsol3
```

```
... ... ... >>> >>> 2.45746688202
```

6.1.7 A simple first order ode evaluated at specific points

Matlab post

We have integrated an ODE over a specific time span. Sometimes it is desirable to get the solution at specific points, e.g. at t = [0 0.2 0.4 0.8]; This could be desirable to compare with experimental measurements at those time points. This example demonstrates how to do that.

$$\frac{dy}{dt} = y(t)$$

The initial condition is y(0) = 1.

```
from scipy.integrate import odeint

y0 = 1
tspan = [0, 0.2, 0.4, 0.8]

def dydt(y, t):
    return y

Y = odeint(dydt, y0, tspan)
print Y[:,0]
```

```
[ 1.          1.22140275  1.49182469  2.22554103]
```

6.1.8 Stopping the integration of an ODE at some condition

Matlab post In Post 968 we learned how to get the numerical solution to an ODE, and then to use the deval function to solve the solution for a particular value. The deval function uses interpolation to evaluate the solution at other valuse. An alternative approach would be to stop the ODE integration when the solution has the value you want. That can be done in Matlab by using an "event" function. You setup an event function and tell the ode solver to use it by setting an option.

Given that the concentration of a species A in a constant volume, batch reactor obeys this differential equation $\frac{dC_A}{dt} = -kC_A^2$ with the initial condition $C_A(t = 0) = 2.3$ mol/L and $k = 0.23$ L/mol/s, compute the time it takes for C_A to be reduced to 1 mol/L.

```
from pycse import *
import numpy as np

k = 0.23
Ca0 = 2.3

```

```
def dCadt(Ca, t):
    return -k * Ca**2

def stop(Ca, t):
    isterminal = True
    direction = 0
    value = 1.0 - Ca
    return value, isterminal, direction

tspan = np.linspace(0.0, 10.0)

t, CA, TE, YE, IE = odelay(dCadt, Ca0, tspan, events=[stop], full_output=1)

print 'At t = {0:1.2f} seconds the concentration of A is {1:1.2f} mol/L.'.format(t[-1], CA[-1])
```

```
At t = 2.46 seconds the concentration of A is 1.00 mol/L.
```

6.1.9 Finding minima and maxima in ODE solutions with events

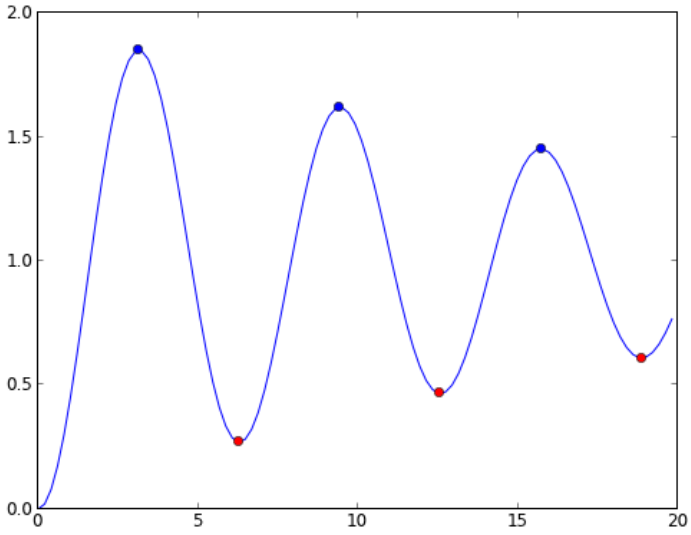
Matlab post Today we look at another way to use events in an ode solver. We use an events function to find minima and maxima, by evaluating the ODE in the event function to find conditions where the first derivative is zero, and approached from the right direction. A maximum is when the fisrt derivative is zero and increasing, and a minimum is when the first derivative is zero and decreasing.

We use a simple ODE, $y' = sin(x) * e^{-0.05x}$, which has minima and maxima.

```
from pycse import *
import numpy as np

def ode(y, x):
    return np.sin(x) * np.exp(-0.05 * x)

def minima(y, x):
    '''Approaching a minumum, dydx is negatime and going to zero. our event function is increasing'''
    value = ode(y, x)
    direction = 1
    isterminal = False
    return value,  isterminal, direction

def maxima(y, x):
    '''Approaching a maximum, dydx is positive and going to zero. our event function is decreasing'''
    value = ode(y, x)
    direction = -1
    isterminal = False
    return value,  isterminal, direction

xspan = np.linspace(0, 20, 100)

y0 = 0

X, Y, XE, YE, IE = odelay(ode, y0, xspan, events=[minima, maxima])
print IE
import matplotlib.pyplot as plt
plt.plot(X, Y)

# blue is maximum, red is minimum
colors = 'rb'
for xe, ye, ie in zip(XE, YE, IE):
    plt.plot([xe], [ye], 'o', color=colors[ie])

```

```
plt.savefig('./images/ode-events-min-max.png')
plt.show()
```

```
[1, 0, 1, 0, 1, 0]
```



6.1.10 Error tolerance in numerical solutions to ODEs

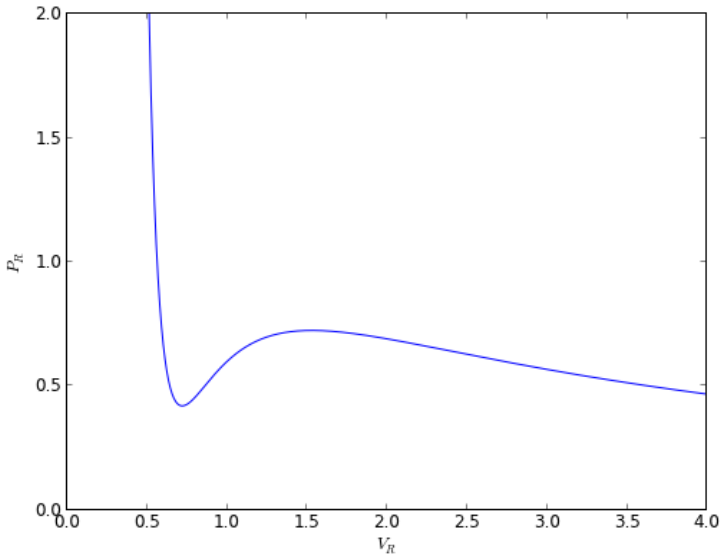
Matlab post Usually, the numerical ODE solvers in python work well with the standard settings. Sometimes they do not, and it is not always obvious they have not worked! Part of using a tool like python is checking how well your solution really worked. We use an example of integrating an ODE that defines the van der Waal equation of an ideal gas here.

we plot the analytical solution to the van der waal equation in reduced form here.

```
import numpy as np
import matplotlib.pyplot as plt

Tr = 0.9
Vr = np.linspace(0.34,4,1000)

#analytical equation for Pr
Prfh = lambda Vr: 8.0 / 3.0 * Tr / (Vr - 1.0 / 3.0) - 3.0 / (Vr**2)
Pr = Prfh(Vr) # evaluated on our reduced volume vector.

# Plot the EOS
plt.plot(Vr,Pr)
plt.ylim([0, 2])
plt.xlabel('$V_R$')
plt.ylabel('$P_R$')
```

```
16  plt.savefig('images/ode-vw-1.png')
17  plt.show()
```

```
>>> >>> >>> >>> >>> ... >>> >>> >>> ... [<matplotlib.lines.Line2D object at 0x1c5a3550>]
(0, 2)
<matplotlib.text.Text object at 0x1c22f750>
<matplotlib.text.Text object at 0x1d4e0750>
```



we want an equation for dPdV, which we will integrate we use symbolic math to do the derivative for us.

```
1  from sympy import diff, Symbol
2  Vrs = Symbol('Vrs')
3
4  Prs = 8.0 / 3.0 * Tr / (Vrs - 1.0/3.0) - 3.0/(Vrs**2)
5  print diff(Prs,Vrs)
```

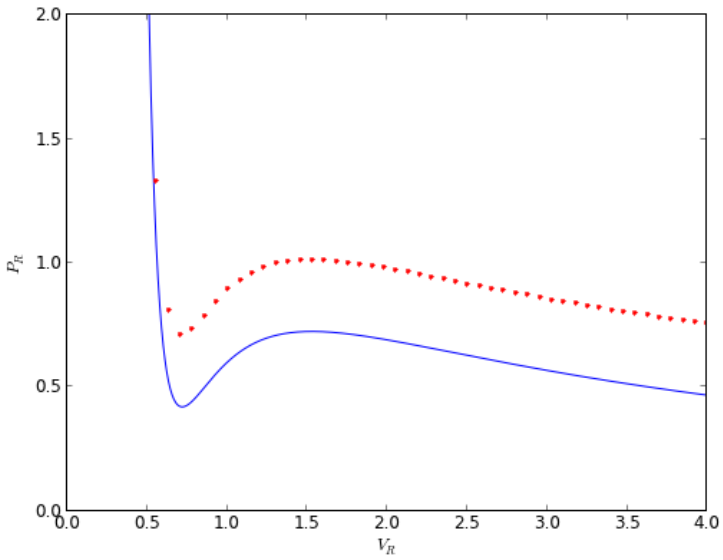
```
>>> -2.4/(Vrs - 0.333333333333333)**2 + 6.0/Vrs**3
```

Now, we solve the ODE. We will specify a large relative tolerance criteria (Note the default is much smaller than what we show here).

```
1  from scipy.integrate import odeint
2
3  def myode(Pr, Vr):
4      dPrdVr = -2.4/(Vr - 0.333333333333333)**2 + 6.0/Vr**3
5      return dPrdVr
```

```

Vspan = np.linspace(0.334, 4)
Po = Prfh(Vspan[0])
P = odeint(myode, Po, Vspan, rtol=1e-4)

# Plot the EOS
plt.plot(Vr,Pr) # analytical solution
plt.plot(Vspan, P[:,0], 'r.')
plt.ylim([0, 2])
plt.xlabel('$V_R$')
plt.ylabel('$P_R$')
plt.savefig('images/ode-vw-2.png')
plt.show()
```

```
... >>> >>> >>> >>> ... [<matplotlib.lines.Line2D object at 0x1d4f3b90>]
[<matplotlib.lines.Line2D object at 0x2ac47518e710>]
(0, 2)
<matplotlib.text.Text object at 0x1c238fd0>
<matplotlib.text.Text object at 0x1c22af10>
```



You can see there is disagreement between the analytical solution and numerical solution. The origin of this problem is accuracy at the initial condition, where the derivative is extremely large.

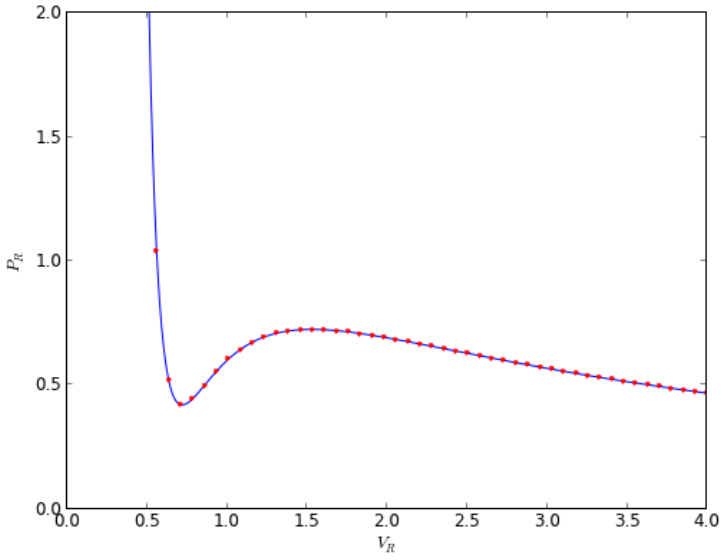
```
print myode(Po, 0.34)
```

```
-53847.3437818
```

We can increase the tolerance criteria to get a better answer. The defaults in odeint are actually set to 1.49012e-8.

```
Vspan = np.linspace(0.334, 4)
Po = Prfh(Vspan[0])
P = odeint(myode, Po, Vspan)

# Plot the EOS
plt.plot(Vr,Pr) # analytical solution
plt.plot(Vspan, P[:,0], 'r.')
plt.ylim([0, 2])
plt.xlabel('$V_R$')
plt.ylabel('$P_R$')
plt.savefig('images/ode-vw-3.png')
plt.show()
```

```
>>> ... [<matplotlib.lines.Line2D object at 0x1d4dbf10>]
[<matplotlib.lines.Line2D object at 0x1c6e5550>]
(0, 2)
<matplotlib.text.Text object at 0x1d4e31d0>
<matplotlib.text.Text object at 0x1d9d3710>
```



The problem here was the derivative value varied by four orders of magnitude over the integration range, so the default tolerances were insufficient to accurately estimate the numerical derivatives over that range. Tightening the tolerances helped resolve that problem. Another approach might be to split the integration up into different regions. For instance, if instead of starting at Vr = 0.34, which is very close to a sigularity in the van der waal equation at Vr = 1/3, if you start at Vr = 0.5, the solution integrates just fine with the standard tolerances.

6.1.11 Solving parameterized ODEs over and over conveniently

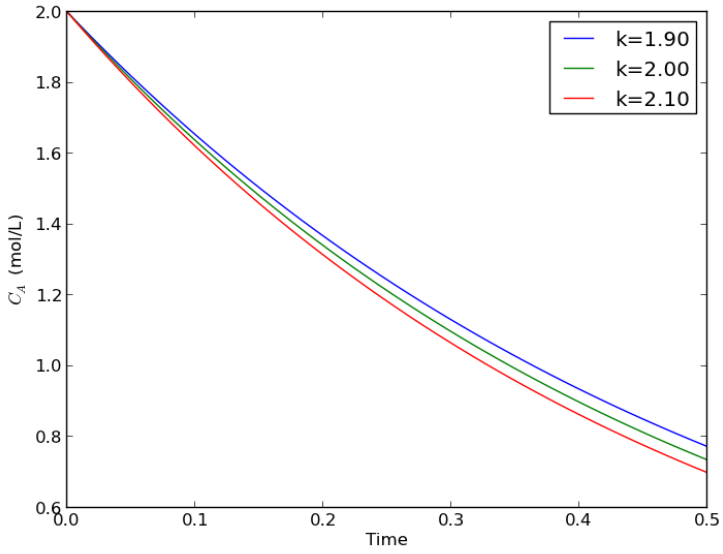
Matlab post Sometimes we have an ODE that depends on a parameter, and we want to solve the ODE for several parameter values. It is inconvenient to write an ode function for each parameter case. Here we examine a convenient way to solve this problem; we pass the parameter to the ODE at runtime. We consider the following ODE:

$$\frac{dCa}{dt} = -kCa(t)$$

where k is a parameter, and we want to solve the equation for a couple of values of k to test the sensitivity of the solution on the parameter. Our question is, given $Ca(t = 0) = 2$, how long does it take to get $Ca = 1$, and how sensitive is the answer to small variations in k?

```
import numpy as np
from scipy.integrate import odeint
import matplotlib.pyplot as plt

def myode(Ca, t, k):
    'ODE definition'
    dCadt = -k * Ca
    return dCadt

tspan = np.linspace(0, 0.5)
k0 = 2
Ca0 = 2

plt.figure(); plt.clf()

for k in [0.95 * k0, k0, 1.05 * k0]:
    sol = odeint(myode, Ca0, tspan, args=(k,))
    plt.plot(tspan, sol, label='k={0:1.2f}'.format(k))
    print 'At t=0.5 Ca = {0:1.2f} mol/L'.format(sol[-1][0])

plt.legend(loc='best')
plt.xlabel('Time')
plt.ylabel('$C_A$ (mol/L)')
plt.savefig('images/parameterized-ode1.png')
```

```
At t=0.5 Ca = 0.77 mol/L
At t=0.5 Ca = 0.74 mol/L
At t=0.5 Ca = 0.70 mol/L
```



You can see there are some variations in the concentration at t = 0.5. You could over or underestimate the concentration if you have the wrong estimate of k! You have to use some judgement here to decide how long to run the reaction to ensure a target goal is met.

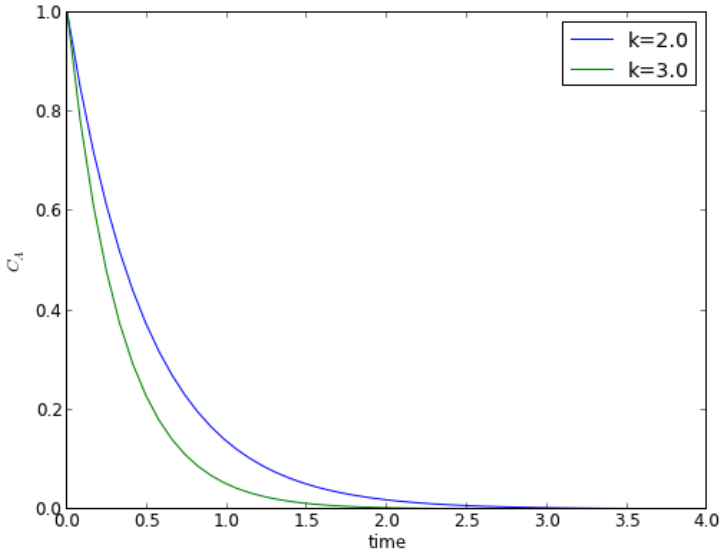
6.1.12 Yet another way to parameterize an ODE

Matlab post We previously examined a way to parameterize an ODE. In those methods, we either used an anonymous function to parameterize an ode function, or we used a nested function that used variables from the shared workspace.

We want a convenient way to solve $dCa/dt = -kCa$ for multiple values of k. Here we use a trick to pass a parameter to an ODE through the initial conditions. We expand the ode function definition to include this parameter, and set its derivative to zero, effectively making it a constant.

```
import numpy as np
from scipy.integrate import odeint
import matplotlib.pyplot as plt

def ode(F, t):
    Ca, k = F
    dCadt = -k * Ca
    dkdt = 0.0
    return [dCadt, dkdt]

tspan = np.linspace(0, 4)

Ca0 = 1;
K = [2.0, 3.0]
for k in K:
    F = odeint(ode, [Ca0, k], tspan)
    Ca = F[:,0]
```

```
18      plt.plot(tspan, Ca, label='k={0}'.format(k))
19  plt.xlabel('time')
20  plt.ylabel('$C_A$')
21  plt.legend(loc='best')
22  plt.savefig('images/ode-parameterized-1.png')
23  plt.show()
```



I do not think this is a very elegant way to pass parameters around compared to the previous methods, but it nicely illustrates that there is more than one way to do it. And who knows, maybe it will be useful in some other context one day!

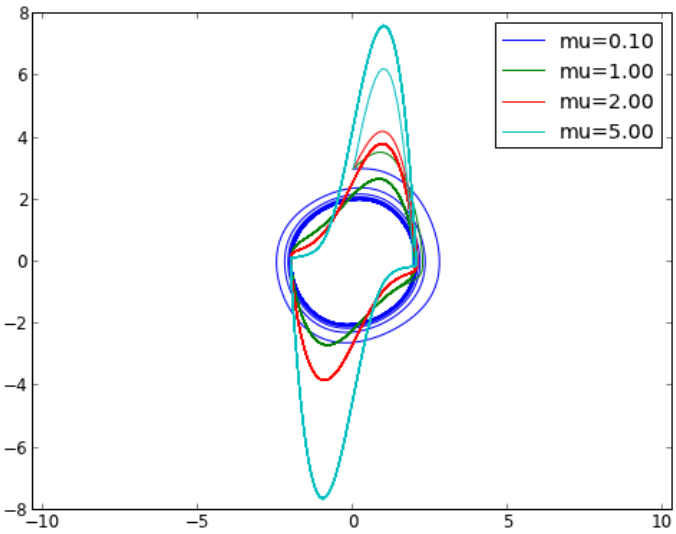
6.1.13 Another way to parameterize an ODE - nested function

Matlab post We saw one method to parameterize an ODE, by creating an ode function that takes an extra parameter argument, and then making a function handle that has the syntax required for the solver, and passes the parameter the ode function.

Here we define the ODE function in a loop. Since the nested function is in the namespace of the main function, it can "see" the values of the variables in the main function. We will use this method to look at the solution to the van der Pol equation for several different values of mu.

```
1  import numpy as np
2  from scipy.integrate import odeint
3  import matplotlib.pyplot as plt
4
5  MU = [0.1, 1, 2, 5]
6  tspan = np.linspace(0, 100, 5000)
7  Y0 = [0, 3]
```

```
8
9   for mu in MU:
10      # define the ODE
11      def vdpol(Y, t):
12          x,y = Y
13          dxdt = y
14          dydt = -x + mu * (1 - x**2) * y
15          return  [dxdt, dydt]
16
17      Y = odeint(vdpol, Y0, tspan)
18
19      x = Y[:,0]; y = Y[:,1]
20      plt.plot(x, y, label='mu={0:1.2f}'.format(mu))
21
22  plt.axis('equal')
23  plt.legend(loc='best')
24  plt.savefig('images/ode-nested-parameterization.png')
25  plt.show()
```



You can see the solution changes dramatically for different values of mu. The point here is not to understand why, but to show an easy way to study a parameterize ode with a nested function. Nested functions can be a great way to "share" variables between functions especially for ODE solving, and nonlinear algebra solving, or any other application where you need a lot of parameters defined in one function in another function.

6.1.14 Solving a second order ode

Matlab post

The odesolvers in scipy can only solve first order ODEs, or systems of first order ODES. To solve a second order ODE, we must convert it by changes of

variables to a system of first order ODES. We consider the Van der Pol oscillator here:

$$\frac{d^2x}{dt^2} - \mu(1 - x^2)\frac{dx}{dt} + x = 0$$

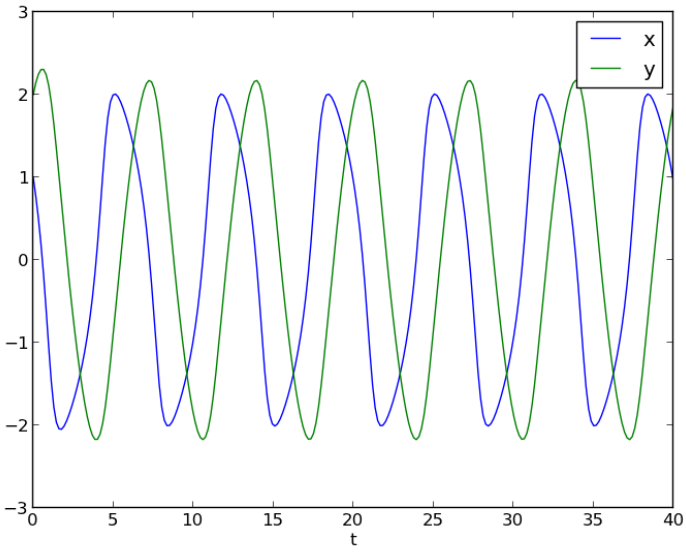
μ is a constant. If we let $y = x - x^3/3$ http://en.wikipedia.org/wiki/Van_der_Pol_oscillator, then we arrive at this set of equations:

$$\frac{dx}{dt} = \mu(x - 1/3x^3 - y)$$

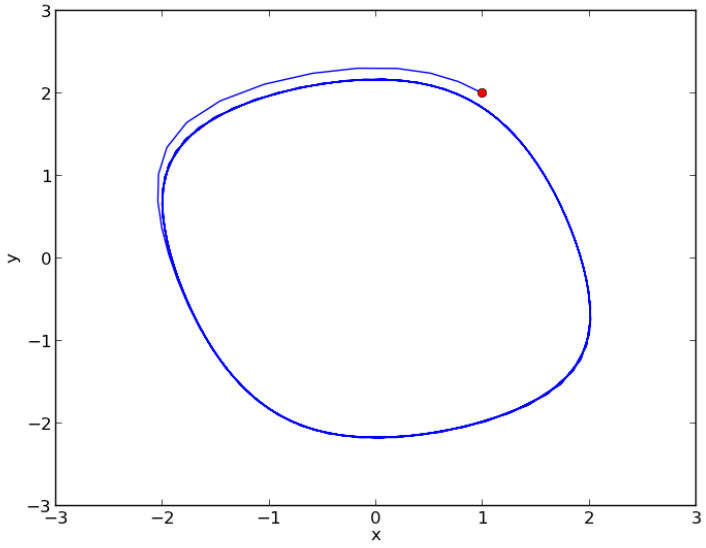
$$\frac{dy}{dt} = \mu/x$$

here is how we solve this set of equations. Let $\mu = 1$.

```
from scipy.integrate import odeint
import numpy as np

mu = 1.0

def vanderpol(X, t):
    x = X[0]
    y = X[1]
    dxdt = mu * (x - 1./3.*x**3 - y)
    dydt = x / mu
    return [dxdt, dydt]

X0 = [1, 2]
t = np.linspace(0, 40, 250)

sol = odeint(vanderpol, X0, t)

import matplotlib.pyplot as plt
x = sol[:, 0]
y = sol[:, 1]

plt.plot(t,x, t, y)
plt.xlabel('t')
plt.legend(('x', 'y'))
plt.savefig('images/vanderpol-1.png')

# phase portrait
plt.figure()
plt.plot(x,y)
plt.plot(x[0], y[0], 'ro')
plt.xlabel('x')
plt.ylabel('y')
plt.savefig('images/vanderpol-2.png')
```



Here is the phase portrait. You can see that a limit cycle is approached, indicating periodicity in the solution.



6.1.15 Solving Bessel's Equation numerically

Matlab post

Reference Ch 5.5 Kreysig, Advanced Engineering Mathematics, 9th ed.

Bessel's equation $x^2y'' + xy' + (x^2 - \nu^2)y = 0$ comes up often in engineering problems such as heat transfer. The solutions to this equation are the Bessel functions. To solve this equation numerically, we must convert it to a system of first order ODEs. This can be done by letting $z = y'$ and $z' = y''$ and performing the change of variables:

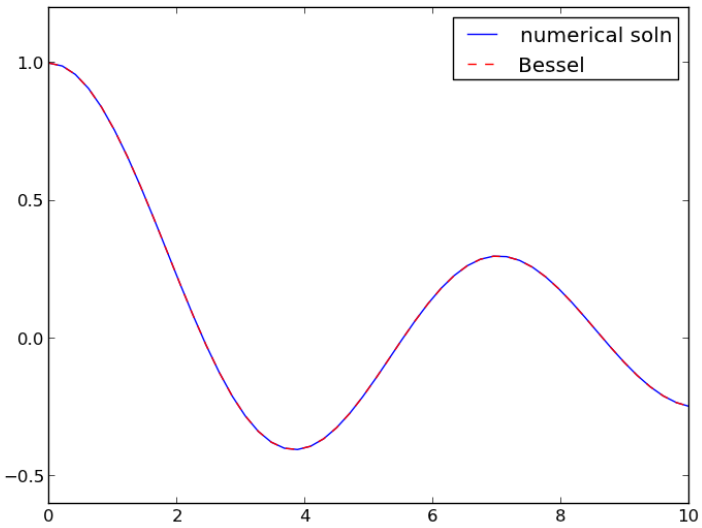
$$y' = z$$

$$z' = \frac{1}{x^2}(-xz - (x^2 - \nu^2)y$$

if we take the case where $\nu = 0$, the solution is known to be the Bessel function $J_0(x)$, which is represented in Matlab as besselj(0,x). The initial conditions for this problem are: $y(0) = 1$ and $y'(0) = 0$.

There is a problem with our system of ODEs at x=0. Because of the $1/x^2$ term, the ODEs are not defined at x=0. If we start very close to zero instead, we avoid the problem.

```
import numpy as np
from scipy.integrate import odeint
from scipy.special import jn # bessel function
import matplotlib.pyplot as plt

def fbessel(Y, x):
    nu = 0.0
    y = Y[0]
    z = Y[1]

    dydx = z
    dzdx = 1.0 / x**2 * (-x * z - (x**2 - nu**2) * y)
    return [dydx, dzdx]

x0 = 1e-15
y0 = 1
z0 = 0
Y0 = [y0, z0]

xspan = np.linspace(1e-15, 10)
sol = odeint(fbessel, Y0, xspan)

plt.plot(xspan, sol[:,0], label='numerical soln')
plt.plot(xspan, jn(0, xspan), 'r--', label='Bessel')
plt.legend()
plt.savefig('images/bessel.png')
```



You can see the numerical and analytical solutions overlap, indicating they are at least visually the same.

6.1.16 Phase portraits of a system of ODEs

Matlab post An undamped pendulum with no driving force is described by

$$y'' + sin(y) = 0$$

We reduce this to standard matlab form of a system of first order ODEs by letting $y_1 = y$ and $y_2 = y_1'$. This leads to:

$y_1' = y_2$

$y_2' = -sin(y_1)$

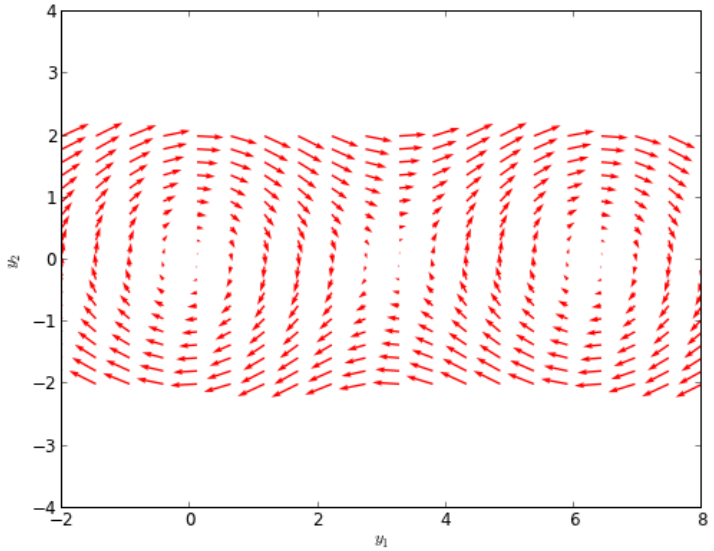
The phase portrait is a plot of a vector field which qualitatively shows how the solutions to these equations will go from a given starting point. here is our definition of the differential equations:

To generate the phase portrait, we need to compute the derivatives y_1' and y_2' at $t = 0$ on a grid over the range of values for y_1 and y_2 we are interested in. We will plot the derivatives as a vector at each (y1, y2) which will show us the initial direction from each point. We will examine the solutions over the range -2 ¡ y1 ¡ 8, and -2 ¡ y2 ¡ 2 for y2, and create a grid of 20 x 20 points.

```
import numpy as np
import matplotlib.pyplot as plt

def f(Y, t):
    y1, y2 = Y
    return [y2, -np.sin(y1)]

```

```
y1 = np.linspace(-2.0, 8.0, 20)
y2 = np.linspace(-2.0, 2.0, 20)

Y1, Y2 = np.meshgrid(y1, y2)

t = 0

u, v = np.zeros(Y1.shape), np.zeros(Y2.shape)

NI, NJ = Y1.shape

for i in range(NI):
    for j in range(NJ):
        x = Y1[i, j]
        y = Y2[i, j]
        yprime = f([x, y], t)
        u[i,j] = yprime[0]
        v[i,j] = yprime[1]


Q = plt.quiver(Y1, Y2, u, v, color='r')

plt.xlabel('$y_1$')
plt.ylabel('$y_2$')
plt.xlim([-2, 8])
plt.ylim([-4, 4])
plt.savefig('images/phase-portrait.png')
```

```
>>> ... >>> >>> >>> >>> >>> >>> ... ... ... >>> >>> <matplotlib.text.Text object at 0xbcfd2
<matplotlib.text.Text object at 0xbd14750>
(-2, 8)
(-4, 4)
```

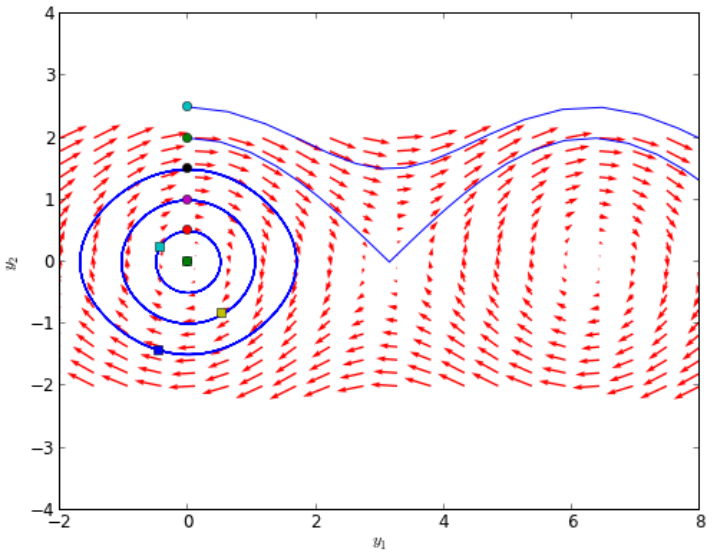


Let us plot a few solutions on the vector field. We will consider the solutions

where y1(0)=0, and values of y2(0) = [0 0.5 1 1.5 2 2.5], in otherwords we start the pendulum at an angle of zero, with some angular velocity.

```
from scipy.integrate import odeint

for y20 in [0, 0.5, 1, 1.5, 2, 2.5]:
    tspan = np.linspace(0, 50, 200)
    y0 = [0.0, y20]
    ys = odeint(f, y0, tspan)
    plt.plot(ys[:,0], ys[:,1], 'b-') # path
    plt.plot([ys[0,0]], [ys[0,1]], 'o') # start
    plt.plot([ys[-1,0]], [ys[-1,1]], 's') # end


plt.xlim([-2, 8])
plt.savefig('images/phase-portrait-2.png')
plt.show()
```

```
>>> ... ... ... [<matplotlib.lines.Line2D object at 0xbc0dbd0>]
[<matplotlib.lines.Line2D object at 0xc135050>]
[<matplotlib.lines.Line2D object at 0xbd1a450>]
[<matplotlib.lines.Line2D object at 0xbd1a1d0>]
[<matplotlib.lines.Line2D object at 0xb88aa10>]
[<matplotlib.lines.Line2D object at 0xb88a5d0>]
[<matplotlib.lines.Line2D object at 0xc14e410>]
[<matplotlib.lines.Line2D object at 0xc14ed90>]
[<matplotlib.lines.Line2D object at 0xc2c5290>]
[<matplotlib.lines.Line2D object at 0xbea4bd0>]
[<matplotlib.lines.Line2D object at 0xbea4d50>]
[<matplotlib.lines.Line2D object at 0xbc401d0>]
[<matplotlib.lines.Line2D object at 0xc2d1190>]
[<matplotlib.lines.Line2D object at 0xc2f3e90>]
[<matplotlib.lines.Line2D object at 0xc2f3bd0>]
[<matplotlib.lines.Line2D object at 0xc2e4790>]
[<matplotlib.lines.Line2D object at 0xc2e0a90>]
[<matplotlib.lines.Line2D object at 0xc2c7390>]
(-2, 8)
```



What do these figures mean? For starting points near the origin, and small velocities, the pendulum goes into a stable limit cycle. For others, the trajectory appears to fly off into y1 space. Recall that y1 is an angle that has values from $-\pi$ to π. The y1 data in this case is not wrapped around to be in this range.

6.1.17 Linear algebra approaches to solving systems of constant coefficient ODEs

Matlab post Today we consider how to solve a system of first order, constant coefficient ordinary differential equations using linear algebra. These equations could be solved numerically, but in this case there are analytical solutions that can be derived. The equations we will solve are:

$y_1' = -0.02y_1 + 0.02y_2$
$y_2' = 0.02y_1 - 0.02y_2$

We can express this set of equations in matrix form as: $\begin{bmatrix} y_1' \\ y_2' \end{bmatrix} = \begin{bmatrix} -0.02 & 0.02 \\ 0.02 & -0.02 \end{bmatrix} \begin{bmatrix} y_1 \\ y_2 \end{bmatrix}$

The general solution to this set of equations is

$$\begin{bmatrix} y_1 \\ y_2 \end{bmatrix} = \begin{bmatrix} v_1 & v_2 \end{bmatrix} \begin{bmatrix} c_1 & 0 \\ 0 & c_2 \end{bmatrix} \exp\left(\begin{bmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{bmatrix} \begin{bmatrix} t \\ t \end{bmatrix} \right)$$

where $\begin{bmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{bmatrix}$ is a diagonal matrix of the eigenvalues of the constant coefficient matrix, $\begin{bmatrix} v_1 & v_2 \end{bmatrix}$ is a matrix of eigenvectors where the i^{th} column corresponds to the eigenvector of the i^{th} eigenvalue, and $\begin{bmatrix} c_1 & 0 \\ 0 & c_2 \end{bmatrix}$ is a matrix

determined by the initial conditions.

In this example, we evaluate the solution using linear algebra. The initial conditions we will consider are $y_1(0) = 0$ and $y_2(0) = 150$.

```
import numpy as np

A = np.array([[-0.02,  0.02],
              [ 0.02, -0.02]])

# Return the eigenvalues and eigenvectors of a Hermitian or symmetric matrix.
evals, evecs = np.linalg.eigh(A)
print evals
print evecs
```

```
>>> ... >>> >>> ... >>> [-0.04  0.  ]
[[ 0.70710678  0.70710678]
 [-0.70710678  0.70710678]]
```

The eigenvectors are the *columns* of evecs.
Compute the c matrix
V*c = Y0

```
Y0 = [0, 150]

c = np.diag(np.linalg.solve(evecs, Y0))
print c
```

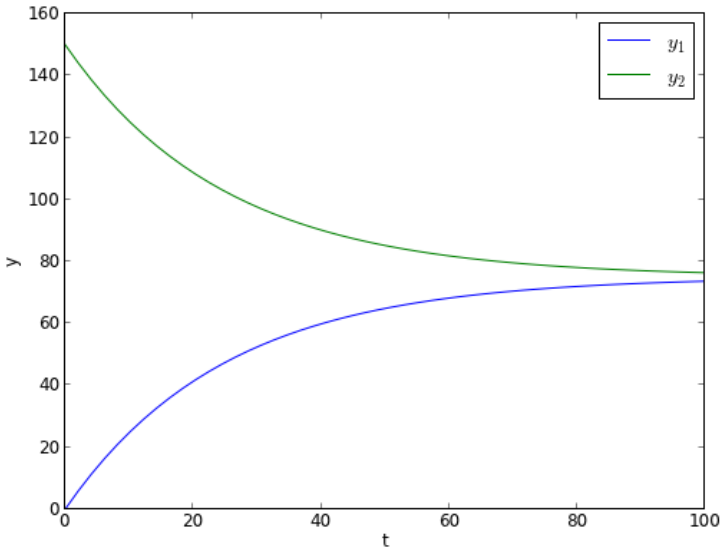
```
>>> >>> [[-106.06601718    0.        ]
 [   0.          106.06601718]]
```

Constructing the solution

We will create a vector of time values, and stack them for each solution, $y_1(t)$ and $Y_2(t)$.

```
import matplotlib.pyplot as plt

t = np.linspace(0, 100)
T = np.row_stack([t, t])

D = np.diag(evals)

# y = V*c*exp(D*T);
y = np.dot(np.dot(evecs, c), np.exp(np.dot(D, T)))

# y has a shape of (2, 50) so we have to transpose it
plt.plot(t, y.T)
plt.xlabel('t')
plt.ylabel('y')
plt.legend(['$y_1$', '$y_2$'])
plt.savefig('images/ode-la.png')
plt.show()
```

```
>>> >>> >>> >>> ... >>> >>> ... [<matplotlib.lines.Line2D object at 0x1d4db950>, <matplotli
<matplotlib.text.Text object at 0x1d35fbd0>
<matplotlib.text.Text object at 0x1c222390>
<matplotlib.legend.Legend object at 0x1d34ee90>
```



6.2 Delay Differential Equations

6.2.1 http://matlab.cheme.cmu.edu/2011/09/28/delay-differential-equations/

6.3 Differential algebraic systems of equations

6.4 Boundary value equations

I am unaware of dedicated BVP solvers in scipy. In the following examples we implement some approaches to solving certain types of linear BVPs.

6.4.1 Plane Poiseuille flow - BVP solve by shooting method

Matlab post

One approach to solving BVPs is to use the shooting method. The reason we cannot use an initial value solver for a BVP is that there is not enough information at the initial value to start. In the shooting method, we take the function value at the initial point, and guess what the function derivatives are so that we can do an integration. If our guess was good, then the solution will go through the known second boundary point. If not, we guess again, until we

get the answer we need. In this example we repeat the pressure driven flow example, but illustrate the shooting method.

In the pressure driven flow of a fluid with viscosity μ between two stationary plates separated by distance d and driven by a pressure drop $\Delta P/\Delta x$, the governing equations on the velocity u of the fluid are (assuming flow in the x-direction with the velocity varying only in the y-direction):

$$\frac{\Delta P}{\Delta x} = \mu \frac{d^2 u}{dy^2}$$

with boundary conditions $u(y = 0) = 0$ and $u(y = d) = 0$, i.e. the no-slip condition at the edges of the plate.

we convert this second order BVP to a system of ODEs by letting $u_1 = u$, $u_2 = u_1'$ and then $u_2' = u_1''$. This leads to:

$\frac{du_1}{dy} = u_2$

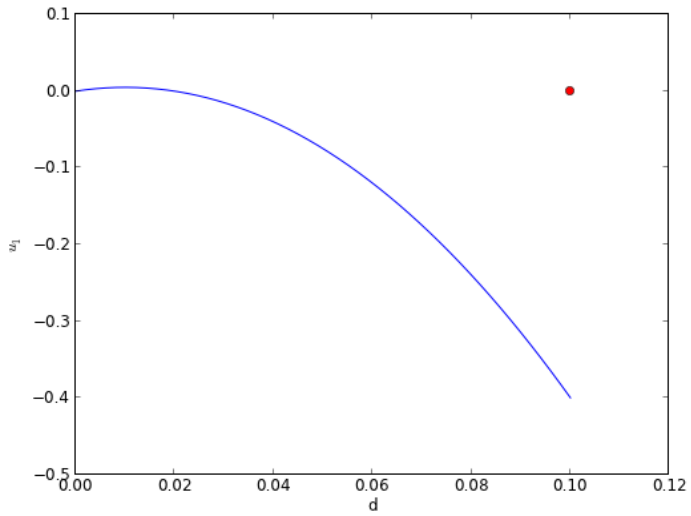
$\frac{du_2}{dy} = \frac{1}{\mu}\frac{\Delta P}{\Delta x}$

with boundary conditions $u_1(y = 0) = 0$ and $u_1(y = d) = 0$.

for this problem we let the plate separation be d=0.1, the viscosity $\mu = 1$, and $\frac{\Delta P}{\Delta x} = -100$.

- First guess
  We need u_1(0) and u_2(0), but we only have u_1(0). We need to guess a value for u_2(0) and see if the solution goes through the u_2(d)=0 boundary value.

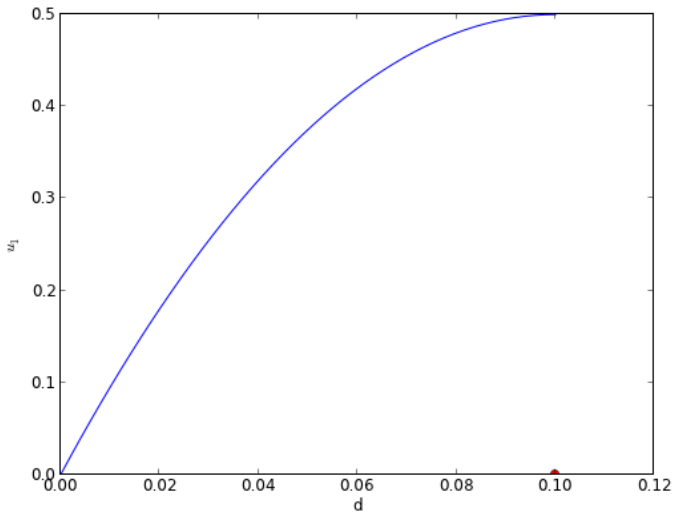
```
import numpy as np
from scipy.integrate import odeint
import matplotlib.pyplot as plt

d = 0.1 # plate thickness

def odefun(U, y):
    u1, u2 = U
    mu = 1
    Pdrop = -100
    du1dy = u2
    du2dy = 1.0 / mu * Pdrop
    return [du1dy, du2dy]

u1_0 = 0 # known
u2_0 = 1 # guessed

dspan = np.linspace(0, d)

U = odeint(odefun, [u1_0, u2_0], dspan)

plt.plot(dspan, U[:,0])
plt.plot([d],[0], 'ro')
plt.xlabel('d')
plt.ylabel('$u_1$')
plt.savefig('images/bvp-shooting-1.png')
```



Here we have undershot the boundary condition. Let us try a larger guess.

- Second guess

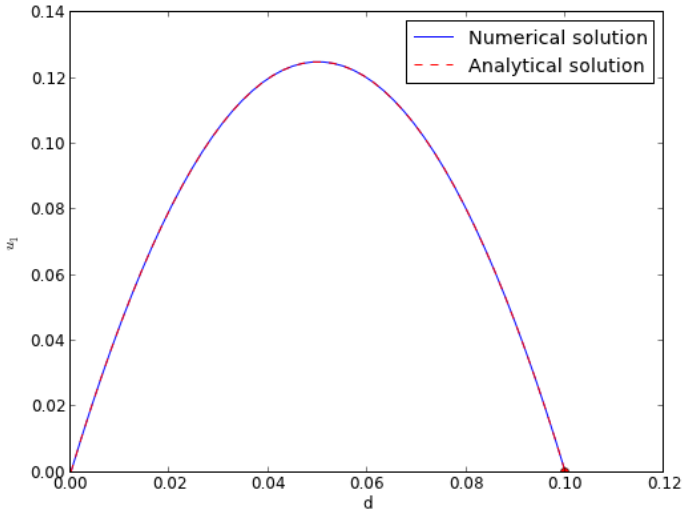
```
import numpy as np
from scipy.integrate import odeint
import matplotlib.pyplot as plt

d = 0.1 # plate thickness

def odefun(U, y):
    u1, u2 = U
    mu = 1
    Pdrop = -100
    du1dy = u2
    du2dy = 1.0 / mu * Pdrop
    return [du1dy, du2dy]

u1_0 = 0 # known
u2_0 = 10 # guessed

dspan = np.linspace(0, d)

U = odeint(odefun, [u1_0, u2_0], dspan)

plt.plot(dspan, U[:,0])
plt.plot([d],[0], 'ro')
plt.xlabel('d')
plt.ylabel('$u_1$')
plt.savefig('images/bvp-shooting-2.png')
```



Now we have clearly overshot. Let us now make a function that will iterate for us to find the right value.

```
import numpy as np
from scipy.integrate import odeint
from scipy.optimize import fsolve
import matplotlib.pyplot as plt

d = 0.1 # plate thickness
Pdrop = -100
mu = 1

def odefun(U, y):
    u1, u2 = U
    du1dy = u2
    du2dy = 1.0 / mu * Pdrop
    return [du1dy, du2dy]

u1_0 = 0 # known
dspan = np.linspace(0, d)

def objective(u2_0):
    dspan = np.linspace(0, d)
    U = odeint(odefun, [u1_0, u2_0], dspan)
    u1 = U[:,0]
    return u1[-1]

u2_0, = fsolve(objective, 1.0)

# now solve with optimal u2_0
U = odeint(odefun, [u1_0, u2_0], dspan)

plt.plot(dspan, U[:,0], label='Numerical solution')
plt.plot([d],[0], 'ro')

# plot an analytical solution
u = -(Pdrop) * d**2 / 2 / mu * (dspan / d - (dspan / d)**2)
plt.plot(dspan, u, 'r--', label='Analytical solution')

```

```
37
38  plt.xlabel('d')
39  plt.ylabel('$u_1$')
40  plt.legend(loc='best')
41  plt.savefig('images/bvp-shooting-3.png')
```



You can see the agreement is excellent!

6.4.2 Plane poiseuelle flow solved by finite difference

Matlab post

Adapted from http://www.physics.arizona.edu/řestrepo/475B/Notes/sourcehtml/node24.html

We want to solve a linear boundary value problem of the form: y" = p(x)y' + q(x)y + r(x) with boundary conditions y(x1) = alpha and y(x2) = beta.

For this example, we solve the plane poiseuille flow problem using a finite difference approach. An advantage of the approach we use here is we do not have to rewrite the second order ODE as a set of coupled first order ODEs, nor do we have to provide guesses for the solution. We do, however, have to discretize the derivatives and formulate a linear algebra problem.

we want to solve u" = 1/mu*DPDX with u(0)=0 and u(0.1)=0. for this problem we let the plate separation be d=0.1, the viscosity $\mu = 1$, and $\frac{\Delta P}{\Delta x} = -100$.

The idea behind the finite difference method is to approximate the derivatives by finite differences on a grid. See here for details. By discretizing the ODE, we arrive at a set of linear algebra equations of the form $Ay = b$, where A and b are defined as follows.

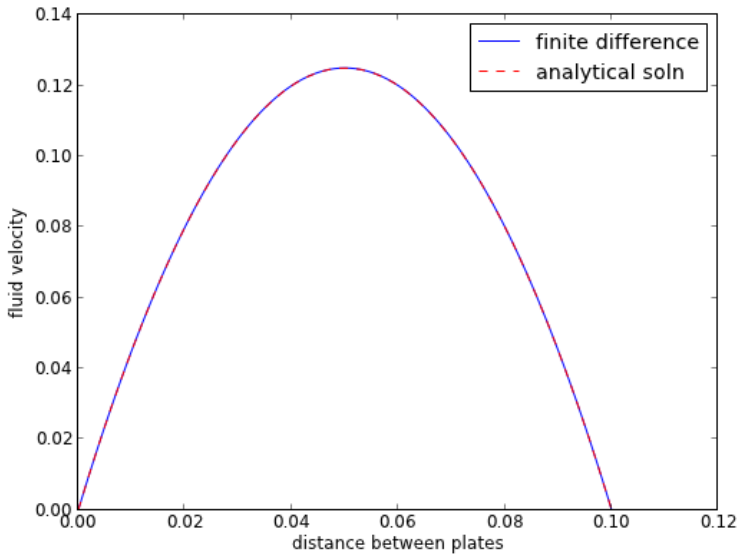
$$A = \begin{bmatrix} 2+h^2q_1 & -1+\frac{h}{2}p_1 & 0 & 0 & 0 \\ -1-\frac{h}{2}p_2 & 2+h^2q_2 & -1+\frac{h}{2}p_2 & 0 & 0 \\ 0 & \ddots & \ddots & \ddots & 0 \\ 0 & 0 & -1-\frac{h}{2}p_{N-1} & 2+h^2q_{N-1} & -1+\frac{h}{2}p_{N-1} \\ 0 & 0 & 0 & -1-\frac{h}{2}p_N & 2+h^2q_N \end{bmatrix}$$

$$y = \begin{bmatrix} y_i \\ \vdots \\ y_N \end{bmatrix}$$

$$b = \begin{bmatrix} -h^2r_1 + (1+\frac{h}{2}p_1)\alpha \\ -h^2r_2 \\ \vdots \\ -h^2r_{N-1} \\ -h^2r_N + (1-\frac{h}{2}p_N)\beta \end{bmatrix}$$

```
import numpy as np

# we use the notation for y'' = p(x)y' + q(x)y + r(x)
def p(x): return 0
def q(x): return 0
def r(x): return -100

#we use the notation y(x1) = alpha and y(x2) = beta

x1 = 0; alpha = 0.0
x2 = 0.1; beta = 0.0

npoints = 100

# compute interval width
h = (x2-x1)/npoints;

# preallocate and shape the b vector and A-matrix
b = np.zeros((npoints - 1, 1));
A = np.zeros((npoints - 1, npoints - 1));
X = np.zeros((npoints - 1, 1));

#now we populate the A-matrix and b vector elements
for i in range(npoints - 1):
    X[i,0] = x1 + (i + 1) * h

    # get the value of the BVP Odes at this x
    pi = p(X[i])
    qi = q(X[i])
    ri = r(X[i])

    if i == 0:
        # first boundary condition
        b[i] = -h**2 * ri + (1 + h / 2 * pi)*alpha;
    elif i == npoints - 1:
        # second boundary condition
        b[i] = -h**2 * ri + (1 - h / 2 * pi)*beta;
    else:
        b[i] = -h**2 * ri # intermediate points

```

```
    for j in range(npoints - 1):
        if j == i: # the diagonal
            A[i,j] = 2 + h**2 * qi
        elif j == i - 1: # left of the diagonal
            A[i,j] = -1 - h / 2 * pi
        elif j == i + 1: # right of the diagonal
            A[i,j] = -1 + h / 2 * pi
        else:
            A[i,j] = 0 # off the tri-diagonal

# solve the equations A*y = b for Y
Y = np.linalg.solve(A,b)

x = np.hstack([x1, X[:,0], x2])
y = np.hstack([alpha, Y[:,0], beta])

import matplotlib.pyplot as plt

plt.plot(x, y)

mu = 1
d = 0.1
x = np.linspace(0,0.1);
Pdrop = -100 # this is DeltaP/Deltax
u = -(Pdrop) * d**2 / 2.0 / mu * (x / d - (x / d)**2)
plt.plot(x,u,'r--')

plt.xlabel('distance between plates')
plt.ylabel('fluid velocity')
plt.legend(('finite difference', 'analytical soln'))
plt.savefig('images/pp-bvp-fd.png')
plt.show()
```



You can see excellent agreement here between the numerical and analytical solution.

6.4.3 http://matlab.cheme.cmu.edu/2011/08/11/plane-poiseuille-flow-bvp/

There is no equivalent of this Matlab function in scipy.

6.4.4 http://matlab.cheme.cmu.edu/2011/08/11/boundary-value-problem-in-heat-conduction/

There is no equivalent of this Matlab function in scipy.

6.5 Partial differential equations

6.5.1 http://matlab.cheme.cmu.edu/2011/08/21/transient-heat-conduction-partial-differential-equations/

I do not think there is a way to do this in scipy.

7 Statistics

7.1 Introduction to statistical data analysis

Matlab post

Given several measurements of a single quantity, determine the average value of the measurements, the standard deviation of the measurements and the 95% confidence interval for the average.

```
import numpy as np

y = [8.1, 8.0, 8.1]

ybar = np.mean(y)
s = np.std(y, ddof=1)

print ybar, s
```

```
>>> >>> >>> >>> >>> >>> 8.06666666667 0.057735026919
```

Interesting, we have to specify the divisor in numpy.std by the ddof argument. The default for this in Matlab is 1, the default for this function is 0.

Here is the principle of computing a confidence interval.

1. compute the average
2. Compute the standard deviation of your data
3. Define the confidence interval, e.g. 95% = 0.95

4. compute the student-t multiplier. This is a function of the confidence interval you specify, and the number of data points you have minus 1. You subtract 1 because one degree of freedom is lost from calculating the average.

The confidence interval is defined as ybar +- T_multiplier*std/sqrt(n).

```
from scipy.stats.distributions import  t
ci = 0.95
alpha = 1.0 - ci

n = len(y)
T_multiplier = t.ppf(1.0 - alpha / 2.0, n - 1)

ci95 = T_multiplier * s / np.sqrt(n)

print 'T_multiplier = {0}'.format(T_multiplier)
print 'ci95 = {0}'.format(ci95)
print 'The true average is between {0} and {1} at a 95% confidence level'.format(ybar - ci95, ybar + ci95)
```

```
>>> >>> >>> >>> >>> >>> >>> >>> T_multiplier = 4.30265272991
ci95 = 0.143421757664
The true average is between 7.923244909 and 8.21008842433 at a 95% confidence level
```

7.2 Basic statistics

Given several measurements of a single quantity, determine the average value of the measurements, the standard deviation of the measurements and the 95% confidence interval for the average.

This is a recipe for computing the confidence interval. The strategy is:

1. compute the average
2. Compute the standard deviation of your data
3. Define the confidence interval, e.g. 95% = 0.95
4. compute the student-t multiplier. This is a function of the confidence

interval you specify, and the number of data points you have minus 1. You subtract 1 because one degree of freedom is lost from calculating the average. The confidence interval is defined as ybar +- T_multiplier*std/sqrt(n).

```
import numpy as np
from scipy.stats.distributions import  t

y = [8.1, 8.0, 8.1]

ybar = np.mean(y)
s = np.std(y)

ci = 0.95
alpha = 1.0 - ci
```

```
11
12  n = len(y)
13  T_multiplier = t.ppf(1-alpha/2.0, n-1)
14
15  ci95 = T_multiplier * s / np.sqrt(n-1)
16
17  print [ybar - ci95, ybar + ci95]
```

```
[7.9232449090029595, 8.210088424330376]
```

We are 95% certain the next measurement will fall in the interval above.

7.3 Confidence interval on an average

`scipy` has a statistical package available for getting statistical distributions. This is useful for computing confidence intervals using the student-t tables. Here is an example of computing a 95% confidence interval on an average.

```
1   import numpy as np
2   from scipy.stats.distributions import  t
3
4   n = 10 # number of measurements
5   dof = n - 1 # degrees of freedom
6   avg_x = 16.1 # average measurement
7   std_x = 0.01 # standard deviation of measurements
8
9   # Find 95% prediction interval for next measurement
10
11  alpha = 1.0 - 0.95
12
13  pred_interval = t.ppf(1-alpha/2., dof) * std_x * np.sqrt(1.0 + 1.0/n)
14
15  s = ['We are 95% confident the next measurement',
16         ' will be between {0:1.3f} and {1:1.3f}']
17  print ''.join(s).format(avg_x - pred_interval, avg_x + pred_interval)
```

```
We are 95% confident the next measurement will be between 16.076 and 16.124
```

7.4 Are averages different

Matlab post

Adapted from http://stattrek.com/ap-statistics-4/unpaired-means.aspx

Class A had 30 students who received an average test score of 78, with standard deviation of 10. Class B had 25 students an average test score of 85, with a standard deviation of 15. We want to know if the difference in these averages is statistically relevant. Note that we only have estimates of the true average and standard deviation for each class, and there is uncertainty in those estimates. As a result, we are unsure if the averages are really different. It could have just been luck that a few students in class B did better.

The hypothesis:

the true averages are the same. We need to perform a two-sample t-test of the hypothesis that $\mu_1 - \mu_2 = 0$ (this is often called the null hypothesis). we use a two-tailed test because we do not care if the difference is positive or negative, either way means the averages are not the same.

```
import numpy as np

n1 = 30  # students in class A
x1 = 78.0  # average grade in class A
s1 = 10.0  # std dev of exam grade in class A

n2 = 25  # students in class B
x2 = 85.0  # average grade in class B
s2 = 15.0  # std dev of exam grade in class B

# the standard error of the difference between the two averages.
SE = np.sqrt(s1**2 / n1 + s2**2 / n2)

# compute DOF
DF = (n1 - 1) + (n2 - 1)
```

see the discussion at http://stattrek.com/Help/Glossary.aspx?Target=Two-sample%20t-test for a more complex definition of degrees of freedom. Here we simply subtract one from each sample size to account for the estimation of the average of each sample.

compute the t-score for our data

The difference between two averages determined from small sample numbers follows the t-distribution. the t-score is the difference between the difference of the means and the hypothesized difference of the means, normalized by the standard error. we compute the absolute value of the t-score to make sure it is positive for convenience later.

```
tscore = np.abs(((x1 - x2) - 0) / SE)
print tscore
```

```
1.99323179108
```

Interpretation

A way to approach determinining if the difference is significant or not is to ask, does our computed average fall within a confidence range of the hypothesized value (zero)? If it does, then we can attribute the difference to statistical variations at that confidence level. If it does not, we can say that statistical variations do not account for the difference at that confidence level, and hence the averages must be different.

Let us compute the t-value that corresponds to a 95% confidence level for a mean of zero with the degrees of freedom computed earlier. This means that 95% of the t-scores we expect to get will fall within $\pm$ t95.

```
from scipy.stats.distributions import  t

ci = 0.95;
alpha = 1 - ci;
t95 = t.ppf(1.0 - alpha/2.0, DF)

print t95
```

```
>>> >>> >>> >>> >>> 2.00574599354
```

since tscore ¡ t95, we conclude that at the 95% confidence level we cannot say these averages are statistically different because our computed t-score falls in the expected range of deviations. Note that our t-score is very close to the 95% limit. Let us consider a smaller confidence interval.

```
ci = 0.94
alpha = 1 - ci;
t95 = t.ppf(1.0 - alpha/2.0, DF)

print t95
```

```
>>> >>> >>> 1.92191364181
```

at the 94% confidence level, however, tscore ¿ t94, which means we can say with 94% confidence that the two averages are different; class B performed better than class A did. Alternatively, there is only about a 6% chance we are wrong about that statement. another way to get there

An alternative way to get the confidence that the averages are different is to directly compute it from the cumulative t-distribution function. We compute the difference between all the t-values less than tscore and the t-values less than -tscore, which is the fraction of measurements that are between them. You can see here that we are practically 95% sure that the averages are different.

```
f = t.cdf(tscore, DF) - t.cdf(-tscore, DF)
print f
```

```
0.948605075732
```

7.5 Model selection

Matlab post

adapted from http://www.itl.nist.gov/div898/handbook/pmd/section4/pmd44.htm

In this example, we show some ways to choose which of several models fit data the best. We have data for the total pressure and temperature of a fixed amount of a gas in a tank that was measured over the course of several days. We want to select a model that relates the pressure to the gas temperature.

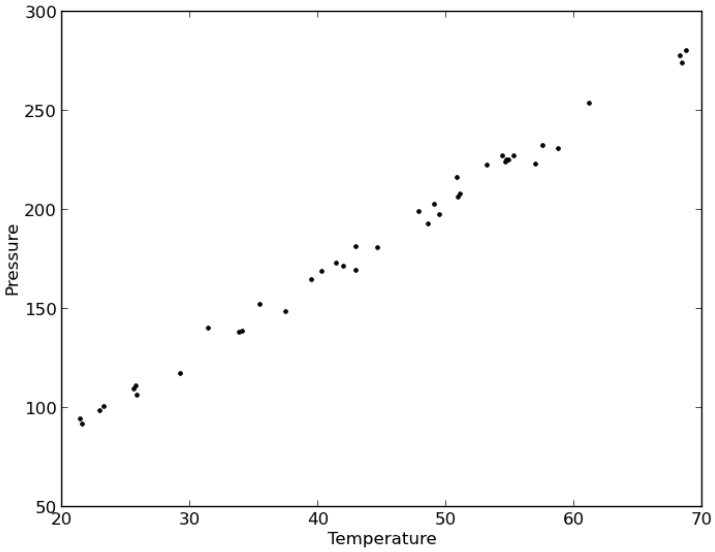
The data is stored in a text file download PT.txt , with the following structure:

```
Run           Ambient                              Fitted
 Order   Day  Temperature   Temperature   Pressure     Value     Residual
   1       1       23.820       54.749       225.066   222.920      2.146
...
```

We need to read the data in, and perform a regression analysis on P vs. T. In python we start counting at 0, so we actually want columns 3 and 4.

```
import numpy as np
import matplotlib.pyplot as plt

data = np.loadtxt('data/PT.txt', skiprows=2)
T = data[:, 3]
P = data[:, 4]

plt.plot(T, P, 'k.')
plt.xlabel('Temperature')
plt.ylabel('Pressure')
plt.savefig('images/model-selection-1.png')
```

```
>>> >>> >>> >>> >>> >>> [<matplotlib.lines.Line2D object at 0x00000000084398D0>]
<matplotlib.text.Text object at 0x000000000841F6A0>
<matplotlib.text.Text object at 0x0000000008423DD8>
```



It appears the data is roughly linear, and we know from the ideal gas law that PV = nRT, or P = nR/V*T, which says P should be linearly correlated with V. Note that the temperature data is in degC, not in K, so it is not expected that P=0 at T = 0. We will use linear algebra to compute the line coefficients.

```
A = np.vstack([T**0, T]).T
b = P

x, res, rank, s = np.linalg.lstsq(A, b)
intercept, slope = x
print 'b, m =', intercept, slope
```

```

n = len(b)
k = len(x)

sigma2 = np.sum((b - np.dot(A,x))**2) / (n - k)

C = sigma2 * np.linalg.inv(np.dot(A.T, A))
se = np.sqrt(np.diag(C))

from scipy.stats.distributions import  t
alpha = 0.05

sT = t.ppf(1-alpha/2., n - k) # student T multiplier
CI = sT * se

print 'CI = ',CI
for beta, ci in zip(x, CI):
    print '[{0} {1}]'.format(beta - ci, beta + ci)
```

```
>>> >>> >>> >>> b, m = 7.74899739238 3.93014043824
>>> >>> >>> >>> >>> >>> >>> >>> >>> >>> >>> >>> >>> >>> >>> CI =  [ 4.76511545  0.1026405 ]
... ... [2.98388194638 12.5141128384]
[3.82749994079 4.03278093569]
```

The confidence interval on the intercept is large, but it does not contain zero at the 95% confidence level.

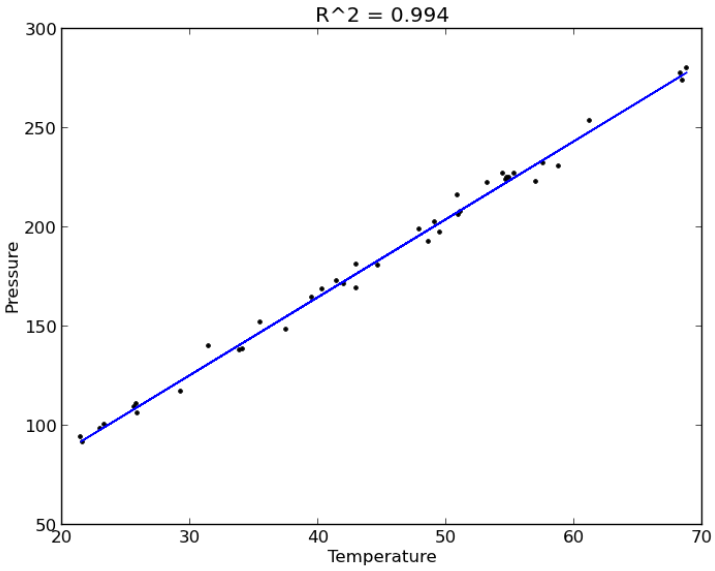
The R^2 value accounts roughly for the fraction of variation in the data that can be described by the model. Hence, a value close to one means nearly all the variations are described by the model, except for random variations.

```
ybar = np.mean(P)
SStot = np.sum((P - ybar)**2)
SSerr = np.sum((P - np.dot(A, x))**2)
R2 = 1 - SSerr/SStot
print R2
```

```
>>> >>> >>> 0.993715411798
```

```
plt.figure(); plt.clf()
plt.plot(T, P, 'k.', T, np.dot(A, x), 'b-')
plt.xlabel('Temperature')
plt.ylabel('Pressure')
plt.title('R^2 = {0:1.3f}'.format(R2))
plt.savefig('images/model-selection-2.png')
```

```
<matplotlib.figure.Figure object at 0x0000000008423860>
[<matplotlib.lines.Line2D object at 0x00000000085BE780>, <matplotlib.lines.Line2D object at
<matplotlib.text.Text object at 0x0000000008449898>
<matplotlib.text.Text object at 0x000000000844CCF8>
<matplotlib.text.Text object at 0x000000000844ED30>
```

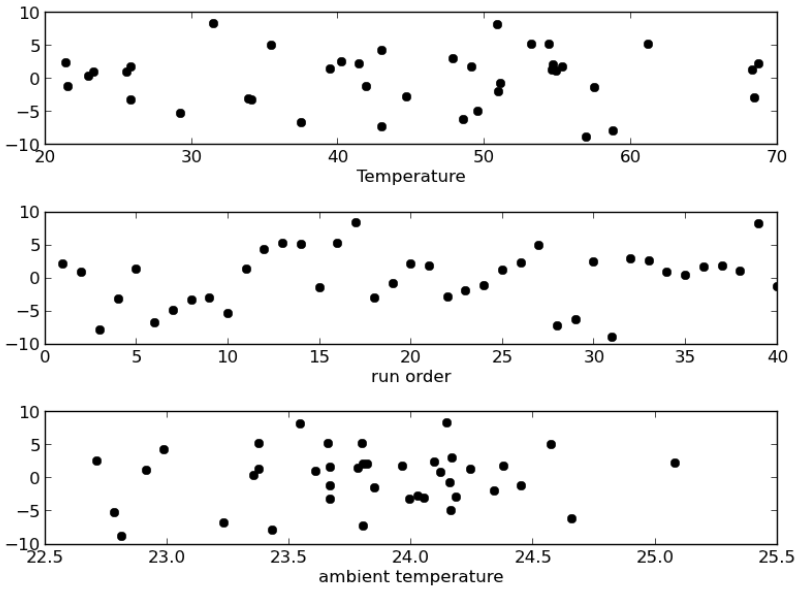


The fit looks good, and R^2 is near one, but is it a good model? There are a few ways to examine this. We want to make sure that there are no systematic trends in the errors between the fit and the data, and we want to make sure there are not hidden correlations with other variables. The residuals are the error between the fit and the data. The residuals should not show any patterns when plotted against any variables, and they do not in this case.

```
residuals = P - np.dot(A, x)

plt.figure()

f, (ax1, ax2, ax3) = plt.subplots(3)

ax1.plot(T,residuals,'ko')
ax1.set_xlabel('Temperature')


run_order = data[:, 0]
ax2.plot(run_order, residuals,'ko ')
ax2.set_xlabel('run order')

ambientT = data[:, 2]
ax3.plot(ambientT, residuals,'ko')
ax3.set_xlabel('ambient temperature')

plt.tight_layout() # make sure plots do not overlap

plt.savefig('images/model-selection-3.png')
```

```
>>> <matplotlib.figure.Figure object at 0x00000000085C21D0>
>>> >>> >>> [<matplotlib.lines.Line2D object at 0x0000000008861CC0>]
<matplotlib.text.Text object at 0x00000000085D3A58>
```

```
>>> >>> >>> [<matplotlib.lines.Line2D object at 0x0000000008861E80>]
<matplotlib.text.Text object at 0x00000000085EC5F8>
>>> >>> [<matplotlib.lines.Line2D object at 0x0000000008861C88>]
<matplotlib.text.Text object at 0x0000000008846828>
```

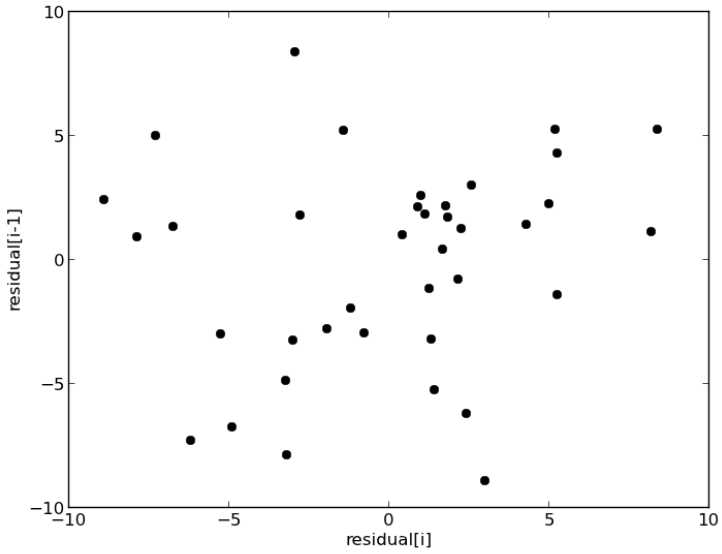


There may be some correlations in the residuals with the run order. That could indicate an experimental source of error.

We assume all the errors are uncorrelated with each other. We can use a lag plot to assess this, where we plot residual[i] vs residual[i-1], i.e. we look for correlations between adjacent residuals. This plot should look random, with no correlations if the model is good.

```
plt.figure(); plt.clf()
plt.plot(residuals[1:-1], residuals[0:-2],'ko')
plt.xlabel('residual[i]')
plt.ylabel('residual[i-1]')
plt.savefig('images/model-selection-correlated-residuals.png')
```

```
<matplotlib.figure.Figure object at 0x000000000886EB00>
[<matplotlib.lines.Line2D object at 0x0000000008A02908>]
<matplotlib.text.Text object at 0x00000000089E8198>
<matplotlib.text.Text object at 0x00000000089EB908>
```



It is hard to argue there is any correlation here.
Lets consider a quadratic model instead.

```
A = np.vstack([T**0, T, T**2]).T
b = P;

x, res, rank, s = np.linalg.lstsq(A, b)
print x

n = len(b)
k = len(x)

sigma2 = np.sum((b - np.dot(A,x))**2) / (n - k)

C = sigma2 * np.linalg.inv(np.dot(A.T, A))
se = np.sqrt(np.diag(C))

from scipy.stats.distributions import  t
alpha = 0.05

sT = t.ppf(1-alpha/2., n - k) # student T multiplier
CI = sT * se

print 'CI = ',CI
for beta, ci in zip(x, CI):
    print '[{0} {1}]'.format(beta - ci, beta + ci)


ybar = np.mean(P)
SStot = np.sum((P - ybar)**2)
SSerr = np.sum((P - np.dot(A,x))**2)
R2 = 1 - SSerr/SStot
print 'R^2 = {0}'.format(R2)
```

```
>>> >>> >>> [  9.00353031e+00   3.86669879e+00   7.26244301e-04]
```

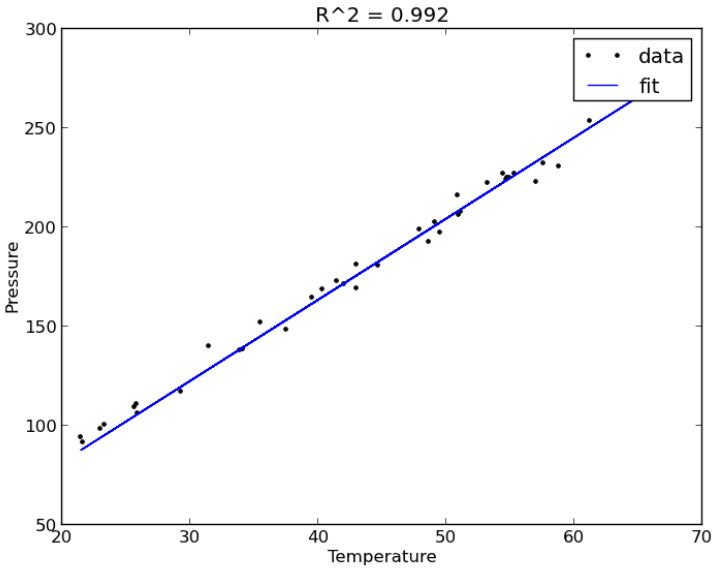
```
>>> >>> >>> >>> >>> >>> >>> >>> >>> >>> >>> >>> >>> >>> >>> CI =  [  1.38030344e+01   6.621
... ... [-4.79950412123 22.8065647329]
[3.20459813681 4.52879944409]
[-0.00675892296907 0.00821141157035]
>>> >>> >>> >>> >>> R^2 = 0.993721969407
```

You can see that the confidence interval on the constant and T^2 term includes zero. That is a good indication this additional parameter is not significant. You can see also that the R^2 value is not better than the one from a linear fit, so adding a parameter does not increase the goodness of fit. This is an example of overfitting the data. Since the constant in this model is apparently not significant, let us consider the simplest model with a fixed intercept of zero.

Let us consider a model with intercept = 0, P = alpha*T.

```
A = np.vstack([T]).T
b = P;

x, res, rank, s = np.linalg.lstsq(A, b)

n = len(b)
k = len(x)

sigma2 = np.sum((b - np.dot(A,x))**2) / (n - k)

C = sigma2 * np.linalg.inv(np.dot(A.T, A))
se = np.sqrt(np.diag(C))

from scipy.stats.distributions import  t
alpha = 0.05

sT = t.ppf(1-alpha/2.0, n - k) # student T multiplier
CI = sT * se

for beta, ci in zip(x, CI):
    print '[{0} {1}]'.format(beta - ci, beta + ci)

plt.figure()
plt.plot(T, P, 'k. ', T, np.dot(A, x))
plt.xlabel('Temperature')
plt.ylabel('Pressure')
plt.legend(['data', 'fit'])

ybar = np.mean(P)
SStot = np.sum((P - ybar)**2)
SSerr = np.sum((P - np.dot(A,x))**2)
R2 = 1 - SSerr/SStot
plt.title('R^2 = {0:1.3f}'.format(R2))
plt.savefig('images/model-selection-no-intercept.png')
```

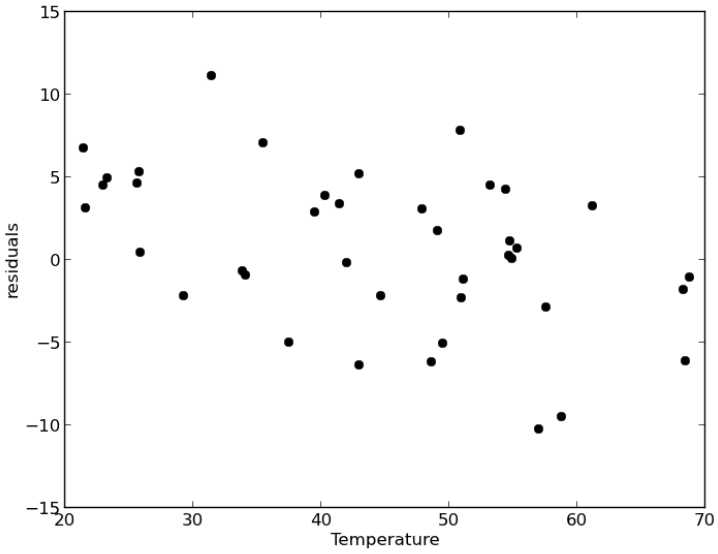
```
>>> >>> >>> >>> >>> >>> >>> >>> >>> >>> >>> >>> >>> >>> >>> >>> >>> >>> >>> ... ... [4.0568012
<matplotlib.figure.Figure object at 0x0000000008870BE0>
[<matplotlib.lines.Line2D object at 0x00000000089F4550>, <matplotlib.lines.Line2D object at
<matplotlib.text.Text object at 0x0000000008A13630>
<matplotlib.text.Text object at 0x0000000008A16DA0>
<matplotlib.legend.Legend object at 0x00000000089EFD30>
>>> >>> >>> >>> >>> <matplotlib.text.Text object at 0x000000000B26C0B8>
```



The fit is visually still pretty good, and the R^2 value is only slightly worse. Let us examine the residuals again.

```
residuals = P - np.dot(A,x)

plt.figure()
plt.plot(T,residuals,'ko')
plt.xlabel('Temperature')
plt.ylabel('residuals')
plt.savefig('images/model-selection-no-incpt-resid.png')
```

```
>>> <matplotlib.figure.Figure object at 0x0000000008A0F5C0>
[<matplotlib.lines.Line2D object at 0x000000000B29B0F0>]
<matplotlib.text.Text object at 0x000000000B276FD0>
<matplotlib.text.Text object at 0x000000000B283780>
```



You can see a slight trend of decreasing value of the residuals as the Temperature increases. This may indicate a deficiency in the model with no intercept. For the ideal gas law in degC: $PV = nR(T+273)$ or $P = nR/V*T+273*nR/V$, so the intercept is expected to be non-zero in this case. Specifically, we expect the intercept to be 273*R*n/V. Since the molar density of a gas is pretty small, the intercept may be close to, but not equal to zero. That is why the fit still looks ok, but is not as good as letting the intercept be a fitting parameter. That is an example of the deficiency in our model.

In the end, it is hard to justify a model more complex than a line in this case.

7.6 Numerical propogation of errors

Matlab post

Propagation of errors is essential to understanding how the uncertainty in a parameter affects computations that use that parameter. The uncertainty propogates by a set of rules into your solution. These rules are not easy to remember, or apply to complicated situations, and are only approximate for equations that are nonlinear in the parameters.

We will use a Monte Carlo simulation to illustrate error propogation. The idea is to generate a distribution of possible parameter values, and to evaluate your equation for each parameter value. Then, we perform statistical analysis on the results to determine the standard error of the results.

We will assume all parameters are defined by a normal distribution with known mean and standard deviation.

7.6.1 Addition and subtraction

```
import numpy as np
import matplotlib.pyplot as plt

N = 1e6 # number of samples of parameters

A_mu = 2.5; A_sigma = 0.4
B_mu = 4.1; B_sigma = 0.3

A = np.random.normal(A_mu, A_sigma, size=(1, N))
B = np.random.normal(B_mu, B_sigma, size=(1, N))

p = A + B
m = A - B

print np.std(p)
print np.std(m)

print np.sqrt(A_sigma**2 + B_sigma**2) # the analytical std dev
```

```
>>> >>> >>> >>> >>> >>> >>> >>> >>> >>> >>> >>> >>> 0.500505424616
0.500113385681
>>> 0.5
```

7.6.2 Multiplication

```
F_mu = 25.0; F_sigma = 1;
x_mu = 6.4; x_sigma = 0.4;

F = np.random.normal(F_mu, F_sigma, size=(1, N))
x = np.random.normal(x_mu, x_sigma, size=(1, N))

t = F * x
print np.std(t)
print np.sqrt((F_sigma / F_mu)**2 + (x_sigma / x_mu)**2) * F_mu * x_mu
```

```
>>> >>> >>> >>> >>> >>> 11.8900166284
11.8726576637
```

7.6.3 Division

This is really like multiplication: F / x = F * (1 / x).

```
d = F / x
print np.std(d)
print np.sqrt((F_sigma / F_mu)**2 + (x_sigma / x_mu)**2) * F_mu / x_mu
```

```
0.293757533168
0.289859806243
```

7.6.4 exponents

This rule is different than multiplication (A^2 = A*A) because in the previous examples we assumed the errors in A and B for A*B were uncorrelated. in A*A, the errors are not uncorrelated, so there is a different rule for error propagation.

```
t_mu = 2.03; t_sigma = 0.01*t_mu; # 1% error
A_mu = 16.07; A_sigma = 0.06;

t = np.random.normal(t_mu, t_sigma, size=(1, N))
A = np.random.normal(A_mu, A_sigma, size=(1, N))

# Compute t^5 and sqrt(A) with error propogation
print np.std(t**5)
print (5 * t_sigma / t_mu) * t_mu**5
```

```
>>> >>> >>> >>> >>> ... 1.72454836176
1.72365440621
```

```
print np.std(np.sqrt(A))
print 1.0 / 2.0 * A_sigma / A_mu * np.sqrt(A_mu)
```

```
0.00748903477329
0.00748364738749
```

7.6.5 the chain rule in error propogation

let v = v0 + a*t, with uncertainties in vo,a and t

```
vo_mu = 1.2; vo_sigma = 0.02;
a_mu = 3.0;  a_sigma  = 0.3;
t_mu = 12.0; t_sigma  = 0.12;

vo = np.random.normal(vo_mu, vo_sigma, (1, N))
a = np.random.normal(a_mu, a_sigma, (1, N))
t = np.random.normal(t_mu, t_sigma, (1, N))

v = vo + a*t

print np.std(v)
print np.sqrt(vo_sigma**2 + t_mu**2 * a_sigma**2 + a_mu**2 * t_sigma**2)
```

```
>>> >>> >>> >>> >>> >>> >>> >>> >>> 3.62232509326
3.61801050303
```

7.6.6 Summary

You can numerically perform error propogation analysis if you know the underlying distribution of errors on the parameters in your equations. One benefit of the numerical propogation is you do not have to remember the error propogation rules, and you directly look at the distribution in nonlinear cases. Some limitations of this approach include

1. You have to know the distribution of the errors in the parameters
2. You have to assume the errors in parameters are uncorrelated.

7.7 Random thoughts

Matlab post

Random numbers are used in a variety of simulation methods, most notably Monte Carlo simulations. In another later example, we will see how we can use random numbers for error propogation analysis. First, we discuss two types of pseudorandom numbers we can use in python: uniformly distributed and normally distributed numbers.

Say you are the gambling type, and bet your friend $5 the next random number will be greater than 0.49. Let us ask Python to roll the random number generator for us.

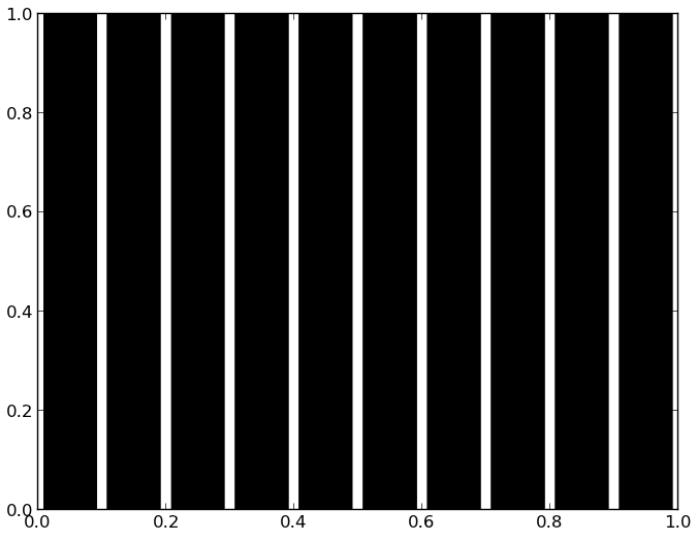
```
import numpy as np

n = np.random.uniform()
print 'n = {0}'.format(n)

if n > 0.49:
    print 'You win!'
else:
    print 'you lose.'
```

```
n = 0.381896986693
you lose.
```

The odds of you winning the last bet are slightly stacked in your favor. There is only a 49% chance your friend wins, but a 51% chance that you win. Lets play the game a lot of times times and see how many times you win, and your friend wins. First, lets generate a bunch of numbers and look at the distribution with a histogram.

```
import numpy as np

N = 10000
games = np.random.uniform(size=(1,N))

wins = np.sum(games > 0.49)
losses = N - wins

print 'You won {0} times ({1:%})'.format(wins, float(wins) / N)

import matplotlib.pyplot as plt
count, bins, ignored = plt.hist(games)
plt.savefig('images/random-thoughts-1.png')
```

```
You won 5090 times (50.900000%)
```



As you can see you win slightly more than you lost.

It is possible to get random integers. Here are a few examples of getting a random integer between 1 and 100. You might do this to get random indices of a list, for example.

```
1  import numpy as np
2
3  print np.random.random_integers(1, 100)
4  print np.random.random_integers(1, 100, 3)
5  print np.random.random_integers(1, 100, (2,2))
```

```
96
[ 95  49 100]
[[69 54]
 [41 93]]
```

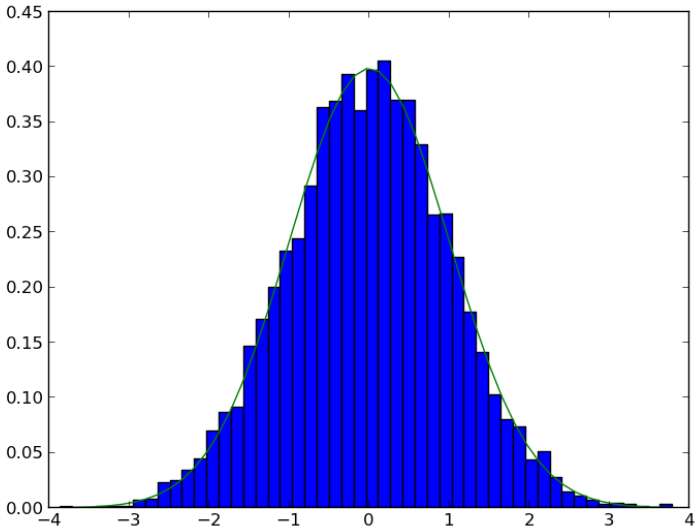
The normal distribution is defined by $f(x) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp(-\frac{(x-\mu)^2}{2\sigma^2})$ where μ is the mean value, and σ is the standard deviation. In the standard distribution, $\mu = 0$ and $\sigma = 1$.

```
1  import numpy as np
2
3  mu = 1
4  sigma = 0.5
5  print np.random.normal(mu, sigma)
6  print np.random.normal(mu, sigma, 2)
```

```
1.04225842065
[ 0.58105204  0.64853157]
```

Let us compare the sampled distribution to the analytical distribution. We generate a large set of samples, and calculate the probability of getting each value using the matplotlib.pyplot.hist command.

```
import numpy as np
import matplotlib.pyplot as plt

mu = 0; sigma = 1

N = 5000
samples = np.random.normal(mu, sigma, N)

counts, bins, ignored = plt.hist(samples, 50, normed=True)

plt.plot(bins, 1.0/np.sqrt(2 * np.pi * sigma**2)*np.exp(-((bins - mu)**2)/(2*sigma**2)))
plt.savefig('images/random-thoughts-2.png')
```



What fraction of points lie between plus and minus one standard deviation of the mean?

samples ¿= mu-sigma will return a vector of ones where the inequality is true, and zeros where it is not. (samples ¿= mu-sigma) & (samples ¡= mu+sigma) will return a vector of ones where there is a one in both vectors, and a zero where there is not. In other words, a vector where both inequalities are true. Finally, we can sum the vector to get the number of elements where the two inequalities are true, and finally normalize by the total number of samples to get the fraction of samples that are greater than -sigma and less than sigma.

```
import numpy as np
import matplotlib.pyplot as plt

mu = 0; sigma = 1
```

```
5
6  N = 5000
7  samples = np.random.normal(mu, sigma, N)
8
9  a = np.sum((samples >= (mu - sigma)) & (samples <= (mu + sigma))) / float(N)
10 b = np.sum((samples >= (mu - 2*sigma)) & (samples <= (mu + 2*sigma))) / float(N)
11 print '{0:%} of samples are within +- standard deviations of the mean'.format(a)
12 print '{0:%} of samples are within +- 2standard deviations of the mean'.format(b)
```

```
67.500000% of samples are within +- standard deviations of the mean
95.580000% of samples are within +- 2standard deviations of the mean
```

7.7.1 Summary

We only considered the numpy.random functions here, and not all of them. There are many distributions of random numbers to choose from. There are also random numbers in the python random module. Remember these are only pseudorandom numbers, but they are still useful for many applications.

8 Data analysis

8.1 Fit a line to numerical data

Matlab post

We want to fit a line to this data:

```
1  x = [0, 0.5, 1, 1.5, 2.0, 3.0, 4.0, 6.0, 10]
2  y = [0, -0.157, -0.315, -0.472, -0.629, -0.942, -1.255, -1.884, -3.147]
```

We use the polyfit(x, y, n) command where n is the polynomial order, n=1 for a line.

```
1  import numpy as np
2
3  p = np.polyfit(x, y, 1)
4  print p
5  slope, intercept = p
6  print slope, intercept
```

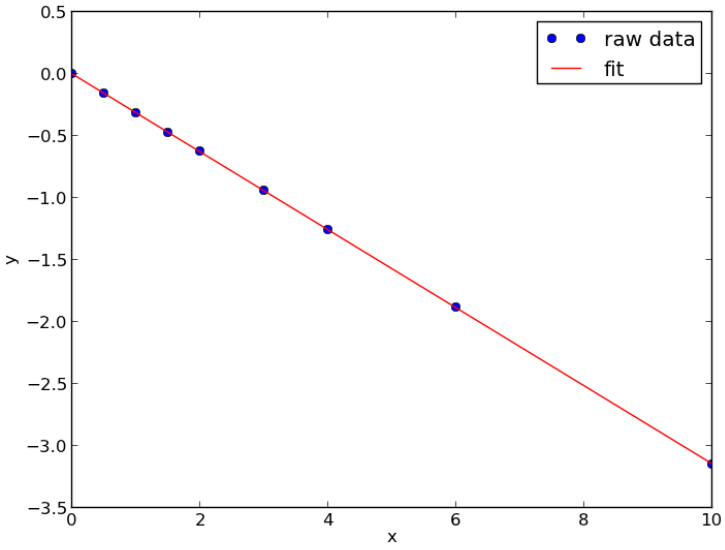
```
>>> >>> [-0.31452218  0.00062457]
>>> -0.3145221843 0.00062457337884
```

To show the fit, we can use numpy.polyval to evaluate the fit at many points.

```
1  import matplotlib.pyplot as plt
2
3  xfit = np.linspace(0, 10)
4  yfit = np.polyval(p, xfit)
5
6  plt.plot(x, y, 'bo', label='raw data')
```

```
7   plt.plot(xfit, yfit, 'r-', label='fit')
8   plt.xlabel('x')
9   plt.ylabel('y')
10  plt.legend()
11  plt.savefig('images/linefit-1.png')
```

```
>>> >>> >>> >>> [<matplotlib.lines.Line2D object at 0x053C1790>]
[<matplotlib.lines.Line2D object at 0x0313C610>]
<matplotlib.text.Text object at 0x052A4950>
<matplotlib.text.Text object at 0x052B9A10>
<matplotlib.legend.Legend object at 0x053C1CD0>
```



8.2 Linear least squares fitting with linear algebra

Matlab post

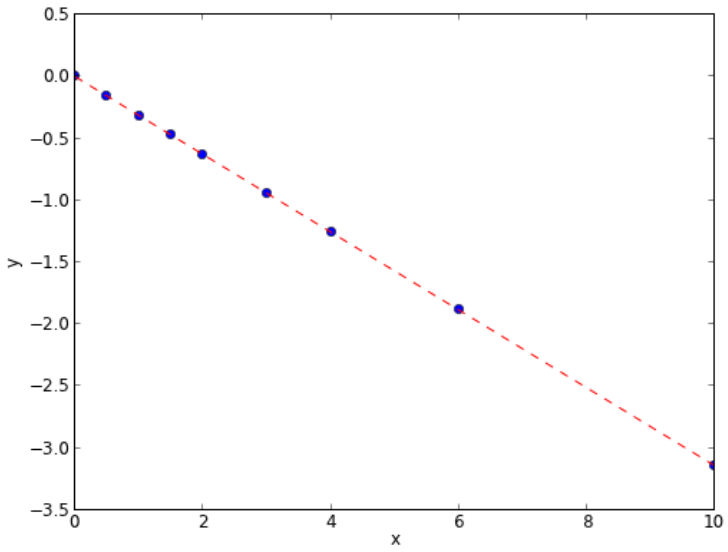
The idea here is to formulate a set of linear equations that is easy to solve. We can express the equations in terms of our unknown fitting parameters p_i as:

```
x1^0*p0 + x1*p1 = y1
x2^0*p0 + x2*p1 = y2
x3^0*p0 + x3*p1 = y3
etc...
```

Which we write in matrix form as $Ap = y$ where A is a matrix of column vectors, e.g. [1, x_i]. A is not a square matrix, so we cannot solve it as written. Instead, we form $A^T Ap = A^T y$ and solve that set of equations.

```
import numpy as np
x = np.array([0, 0.5, 1, 1.5, 2.0, 3.0, 4.0, 6.0, 10])
y = np.array([0, -0.157, -0.315, -0.472, -0.629, -0.942, -1.255, -1.884, -3.147])

A = np.column_stack([x**0, x])

M = np.dot(A.T, A)
b = np.dot(A.T, y)

i1, slope1 = np.dot(np.linalg.inv(M), b)
i2, slope2 = np.linalg.solve(M, b) # an alternative approach.

print i1, slope1
print i2, slope2

# plot data and fit
import matplotlib.pyplot as plt

plt.plot(x, y, 'bo')
plt.plot(x, np.dot(A, [i1, slope1]), 'r--')
plt.xlabel('x')
plt.ylabel('y')
plt.savefig('images/la-line-fit.png')
```

```
0.00062457337884 -0.3145221843
0.00062457337884 -0.3145221843
```



This method can be readily extended to fitting any polynomial model, or other linear model that is fit in a least squares sense. This method does not provide confidence intervals.

8.3 Linear regression with confidence intervals.

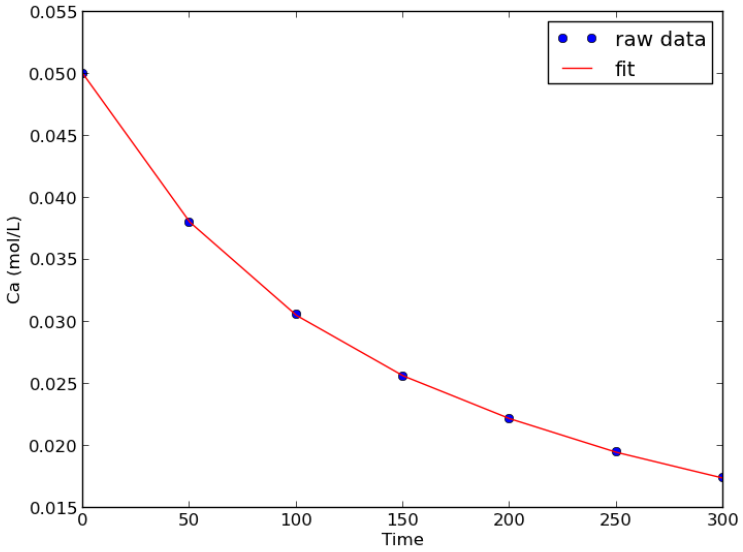
Matlab post Fit a fourth order polynomial to this data and determine the con-

fidence interval for each parameter. Data from example 5-1 in Fogler, Elements of Chemical Reaction Engineering.

We want the equation $Ca(t) = b0 + b1 * t + b2 * t^2 + b3 * t^3 + b4 * t^4$ fit to the data in the least squares sense. We can write this in a linear algebra form as: T*p = Ca where T is a matrix of columns [1 t t^2 t^3 t^4], and p is a column vector of the fitting parameters. We want to solve for the p vector and estimate the confidence intervals.

```
import numpy as np
from scipy.stats.distributions import  t

time = np.array([0.0, 50.0, 100.0, 150.0, 200.0, 250.0, 300.0])
Ca = np.array([50.0, 38.0, 30.6, 25.6, 22.2, 19.5, 17.4])*1e-3

T = np.column_stack([time**0, time, time**2, time**3, time**4])

p, res, rank, s = np.linalg.lstsq(T, Ca)
# the parameters are now in p

# compute the confidence intervals
n = len(Ca)
k = len(p)

sigma2 = np.sum((Ca - np.dot(T, p))**2) / (n - k)  # RMSE

C = sigma2 * np.linalg.inv(np.dot(T.T, T)) # covariance matrix
se = np.sqrt(np.diag(C)) # standard error

alpha = 0.05 # 100*(1 - alpha) confidence level

sT = t.ppf(1.0 - alpha/2.0, n - k) # student T multiplier
CI = sT * se

for beta, ci in zip(p, CI):
    print '{2: 1.2e} [{0: 1.4e} {1: 1.4e}]'.format(beta - ci, beta + ci, beta)

SS_tot = np.sum((Ca - np.mean(Ca))**2)
SS_err = np.sum((np.dot(T, p) - Ca)**2)

#  http://en.wikipedia.org/wiki/Coefficient_of_determination
Rsq = 1 - SS_err/SS_tot
print 'R^2 = {0}'.format(Rsq)

# plot fit
import matplotlib.pyplot as plt
plt.plot(time, Ca, 'bo', label='raw data')
plt.plot(time, np.dot(T, p), 'r-', label='fit')
plt.xlabel('Time')
plt.ylabel('Ca (mol/L)')
plt.legend(loc='best')
plt.savefig('images/linregress-conf.png')
```

```
 5.00e-02 [ 4.9680e-02  5.0300e-02]
-2.98e-04 [-3.1546e-04 -2.8023e-04]
 1.34e-06 [ 1.0715e-06  1.6155e-06]
-3.48e-09 [-4.9032e-09 -2.0665e-09]
 3.70e-12 [ 1.3501e-12  6.0439e-12]
R^2 = 0.999986967246
```



A fourth order polynomial fits the data well, with a good R^2 value. All of the parameters appear to be significant, i.e. zero is not included in any of the parameter confidence intervals. This does not mean this is the best model for the data, just that the model fits well.

8.4 Fitting a numerical ODE solution to data

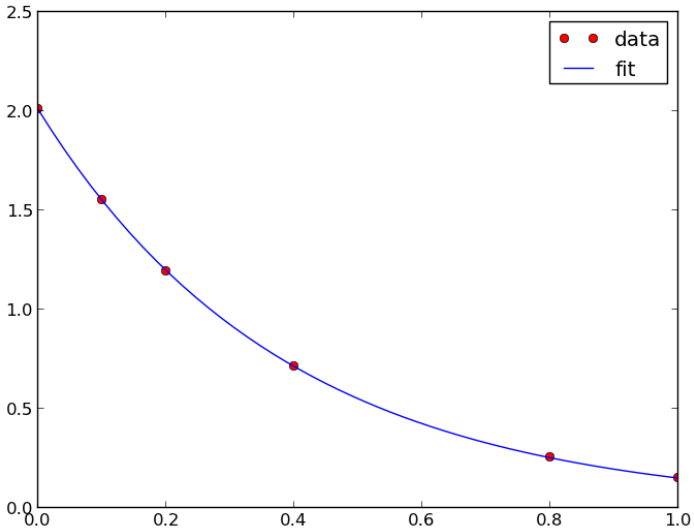
Matlab post

Suppose we know the concentration of A follows this differential equation: $\frac{dC_A}{dt} = -kC_A$, and we have data we want to fit to it. Here is an example of doing that.

```
import numpy as np
from scipy.optimize import curve_fit
from scipy.integrate import odeint

# given data we want to fit
tspan = [0, 0.1, 0.2, 0.4, 0.8, 1]
Ca_data = [2.0081,  1.5512,  1.1903,  0.7160,  0.2562,  0.1495]

def fitfunc(t, k):
    'Function that returns Ca computed from an ODE for a k'
    def myode(Ca, t):
        return -k * Ca

    Ca0 = Ca_data[0]
    Casol = odeint(myode, Ca0, t)
    return Casol[:,0]

k_fit, kcov = curve_fit(fitfunc, tspan, Ca_data, p0=1.3)
print k_fit

tfit = np.linspace(0,1);
```

```
fit = fitfunc(tfit, k_fit)

import matplotlib.pyplot as plt
plt.plot(tspan, Ca_data, 'ro', label='data')
plt.plot(tfit, fit, 'b-', label='fit')
plt.legend(loc='best')
plt.savefig('images/ode-fit.png')
```

```
[ 2.58893455]
```



8.5 Nonlinear curve fitting

Here is a typical nonlinear function fit to data. you need to provide an initial guess. In this example we fit the Birch-Murnaghan equation of state to energy vs. volume data from density functional theory calculations.

```
from scipy.optimize import leastsq
import numpy as np

vols = np.array([13.71, 14.82, 16.0, 17.23, 18.52])

energies = np.array([-56.29, -56.41, -56.46, -56.463, -56.41])

def Murnaghan(parameters, vol):
    'From Phys. Rev. B 28, 5480 (1983)'
    E0, B0, BP, V0 = parameters

    E = E0 + B0 * vol / BP * (((V0 / vol)**BP) / (BP - 1) + 1) - V0 * B0 / (BP - 1.0)

    return E

def objective(pars, y, x):
```

```
    #we will minimize this function
    err =  y - Murnaghan(pars, x)
    return err

x0 = [ -56.0, 0.54, 2.0, 16.5] #initial guess of parameters

plsq = leastsq(objective, x0, args=(energies, vols))

print 'Fitted parameters = {0}'.format(plsq[0])

import matplotlib.pyplot as plt
plt.plot(vols,energies, 'ro')

#plot the fitted curve on top
x = np.linspace(min(vols), max(vols), 50)
y = Murnaghan(plsq[0], x)
plt.plot(x, y, 'k-')
plt.xlabel('Volume')
plt.ylabel('Energy')
plt.savefig('images/nonlinear-curve-fitting.png')
```

```
Fitted parameters = [-56.46839641   0.57233217   2.7407944   16.55905648]
```

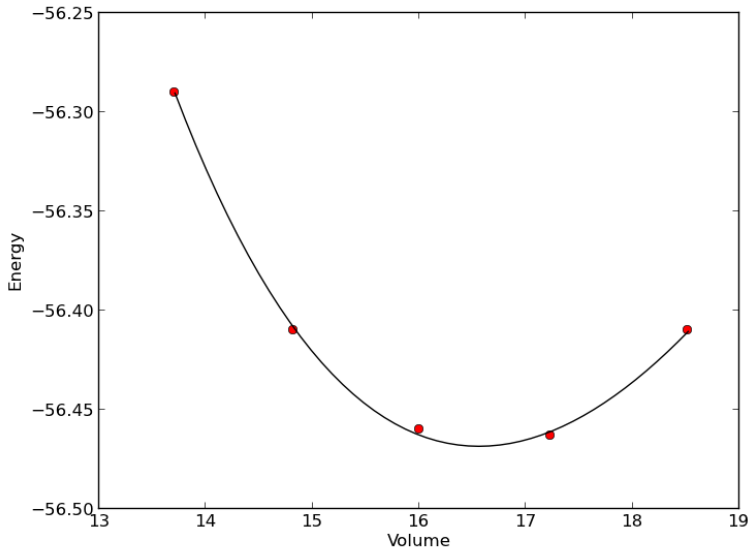


Figure 1: Example of least-squares non-linear curve fitting.

See additional examples at [[http://docs.scipy.org/doc/scipy/reference/tutorial/optimize.html][http://docs.scipy.org/doc/scipy/reference/tutorial/optimize.html]].

8.6 Graphical methods to help get initial guesses for multivariate nonlinear regression

Matlab post

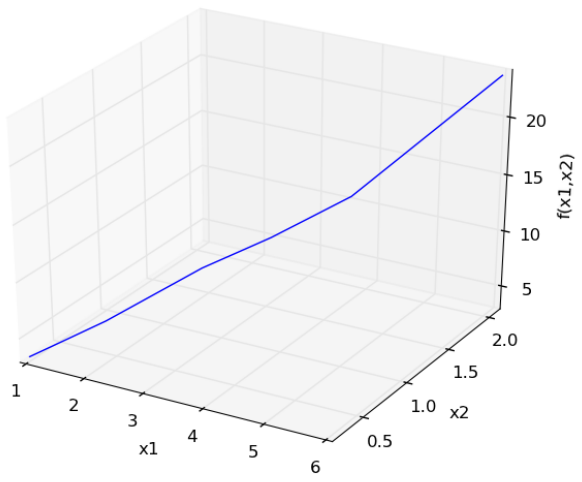
Fit the model f(x1,x2; a,b) = a*x1 + x2^b to the data given below. This model has two independent variables, and two parameters.

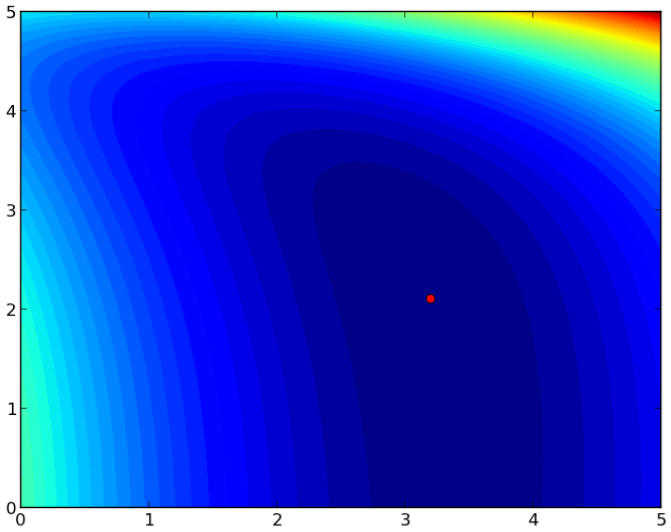
We want to do a nonlinear fit to find a and b that minimize the summed squared errors between the model predictions and the data. With only two variables, we can graph how the summed squared error varies with the parameters, which may help us get initial guesses. Let us assume the parameters lie in a range, here we choose 0 to 5. In other problems you would adjust this as needed.

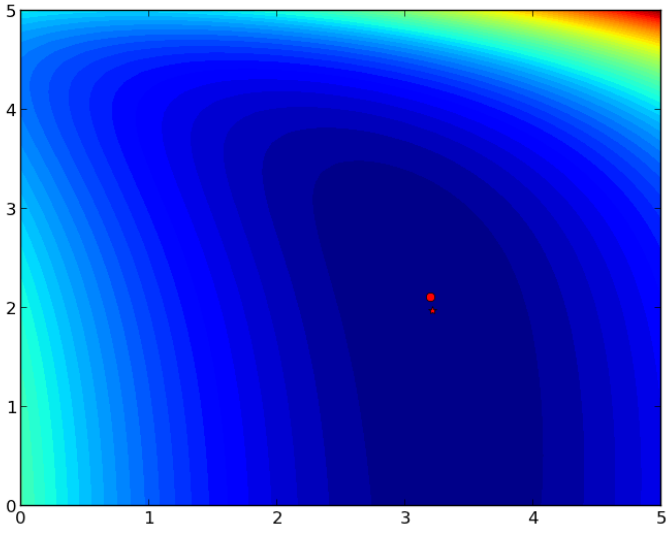
```
import numpy as np
from mpl_toolkits.mplot3d import Axes3D
import matplotlib.pyplot as plt

x1 = [1.0, 2.0, 3.0, 4.0, 5.0, 6.0]
x2 = [0.2, 0.4, 0.8, 0.9, 1.1, 2.1]
X = np.column_stack([x1, x2]) # independent variables

f = [ 3.3079,    6.6358,   10.3143,   13.6492,   17.2755,   23.6271]

fig = plt.figure()
ax = fig.gca(projection = '3d')

ax.plot(x1, x2, f)
ax.set_xlabel('x1')
ax.set_ylabel('x2')
ax.set_zlabel('f(x1,x2)')

plt.savefig('images/graphical-mulvar-1.png')


arange = np.linspace(0,5);
brange = np.linspace(0,5);

A,B = np.meshgrid(arange, brange)

def model(X, a, b):
    'Nested function for the model'
    x1 = X[:, 0]
    x2 = X[:, 1]

    f = a * x1 + x2**b
    return f

@np.vectorize
def errfunc(a, b):
    # function for the summed squared error
    fit = model(X, a, b)
    sse = np.sum((fit - f)**2)
    return sse

SSE = errfunc(A, B)

plt.clf()
plt.contourf(A, B, SSE, 50)
plt.plot([3.2], [2.1], 'ro')
plt.figtext( 3.4, 2.2, 'Minimum near here', color='r')

plt.savefig('images/graphical-mulvar-2.png')

guesses = [3.18, 2.02]
```

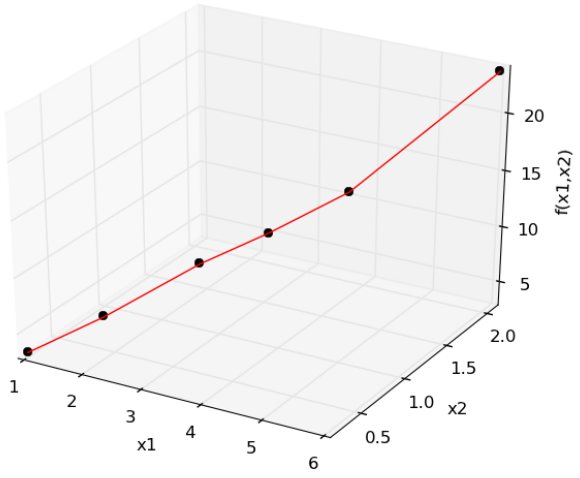
```
52
53  from scipy.optimize import curve_fit
54
55  popt, pcov = curve_fit(model, X, f, guesses)
56  print popt
57
58  plt.plot([popt[0]], [popt[1]], 'r*')
59  plt.savefig('images/graphical-mulvar-3.png')
60
61  print model(X, *popt)
62
63  fig = plt.figure()
64  ax = fig.gca(projection = '3d')
65
66  ax.plot(x1, x2, f, 'ko', label='data')
67  ax.plot(x1, x2, model(X, *popt), 'r-', label='fit')
68  ax.set_xlabel('x1')
69  ax.set_ylabel('x2')
70  ax.set_zlabel('f(x1,x2)')
71
72  plt.savefig('images/graphical-mulvar-4.png')
```

```
[ 3.21694798  1.9728254 ]
[  3.25873623   6.59792994  10.29473657  13.68011436  17.29161001
  23.62366445]
```




0
1
2
3
4
5
0
1
2
3
4
5


0
1
2
3
4
5
0
1
2
3
4
5



It can be difficult to figure out initial guesses for nonlinear fitting problems. For one and two dimensional systems, graphical techniques may be useful to visualize how the summed squared error between the model and data depends on the parameters.

8.7 Nonlinear curve fitting by direct least squares minimization

Here is an example of fitting a nonlinear function to data by direct minimization of the summed squared error.

```
from scipy.optimize import fmin
import numpy as np

volumes = np.array([13.71, 14.82, 16.0, 17.23, 18.52])

energies = np.array([-56.29, -56.41, -56.46, -56.463,-56.41])

def Murnaghan(parameters,vol):
    'From PRB 28,5480 (1983'
    E0 = parameters[0]
    B0 = parameters[1]
    BP = parameters[2]
    V0 = parameters[3]

    E = E0 + B0*vol/BP*(((V0/vol)**BP)/(BP-1)+1) - V0*B0/(BP-1.)

    return E

def objective(pars,vol):
    #we will minimize this function
    err =  energies - Murnaghan(pars,vol)
    return np.sum(err**2) #we return the summed squared error directly
```

```
23
24  x0 = [ -56., 0.54, 2., 16.5] #initial guess of parameters
25
26  plsq = fmin(objective,x0,args=(volumes,)) #note args is a tuple
27
28  print 'parameters = {0}'.format(plsq)
29
30  import matplotlib.pyplot as plt
31  plt.plot(volumes,energies,'ro')
32
33  #plot the fitted curve on top
34  x = np.linspace(min(volumes),max(volumes),50)
35  y = Murnaghan(plsq,x)
36  plt.plot(x,y,'k-')
37  plt.xlabel('Volume ($\AA^3$)')
38  plt.ylabel('Total energy (eV)')
39  plt.savefig('images/nonlinear-fitting-lsq.png')
```

```
Optimization terminated successfully.
         Current function value: 0.000020
         Iterations: 137
         Function evaluations: 240
parameters = [-56.46932645   0.59141447   1.9044796   16.59341303]
```

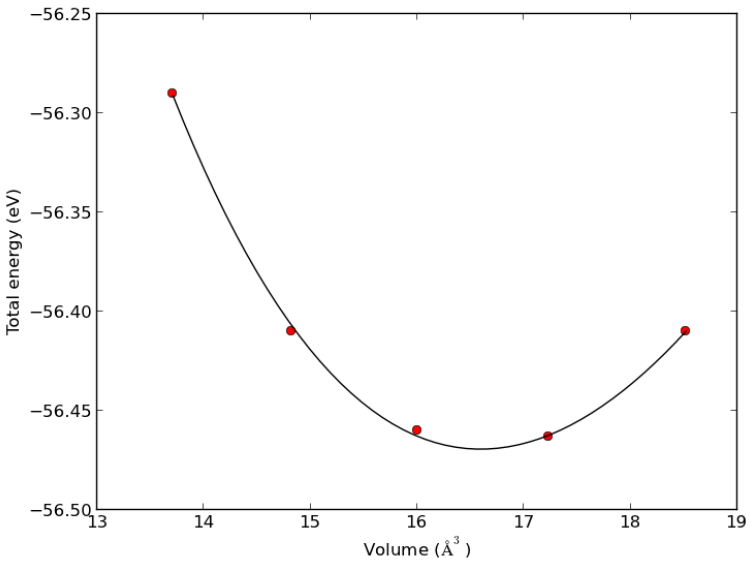


Figure 2: Fitting a nonlinear function.

8.8 Nonlinear curve fitting with parameter confidence intervals

Matlab post

We often need to estimate parameters from nonlinear regression of data. We should also consider how good the parameters are, and one way to do that is to consider the confidence interval. A confidence interval tells us a range that we are confident the true parameter lies in.

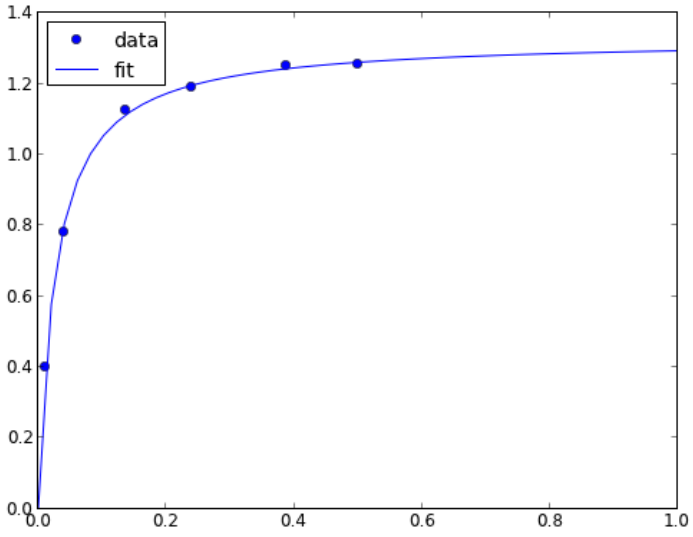
In this example we use a nonlinear curve-fitting function: scipy.optimize.curve_fit to give us the parameters in a function that we define which best fit the data. The scipy.optimize.curve_fit function also gives us the covariance matrix which we can use to estimate the standard error of each parameter. Finally, we modify the standard error by a student-t value which accounts for the additional uncertainty in our estimates due to the small number of data points we are fitting to.

We will fit the function $y = ax/(b + x)$ to some data, and compute the 95% confidence intervals on the parameters.

```
# Nonlinear curve fit with confidence interval
import numpy as np
from scipy.optimize import curve_fit
from scipy.stats.distributions import  t

x = np.array([0.5, 0.387, 0.24, 0.136, 0.04, 0.011])
y = np.array([1.255, 1.25, 1.189, 1.124, 0.783, 0.402])

# this is the function we want to fit to our data
def func(x, a, b):
    'nonlinear function in a and b to fit to data'
    return a * x / (b + x)

initial_guess = [1.2, 0.03]
pars, pcov = curve_fit(func, x, y, p0=initial_guess)

alpha = 0.05 # 95% confidence interval = 100*(1-alpha)

n = len(y)    # number of data points
p = len(pars) # number of parameters

dof = max(0, n - p) # number of degrees of freedom

# student-t value for the dof and confidence level
tval = t.ppf(1.0-alpha/2., dof)

for i, p,var in zip(range(n), pars, np.diag(pcov)):
    sigma = var**0.5
    print 'p{0}: {1} [{2}  {3}]'.format(i, p,
                                  p - sigma*tval,
                                  p + sigma*tval)

import matplotlib.pyplot as plt
plt.plot(x,y,'bo ')
xfit = np.linspace(0,1)
yfit = func(xfit, pars[0], pars[1])
plt.plot(xfit,yfit,'b-')
plt.legend(['data','fit'],loc='best')
plt.savefig('images/nonlin-curve-fit-ci.png')
```

```
p0: 1.32753141454 [1.3005365922  1.35452623688]
```

```
p1: 0.0264615569701 [0.0236076538292  0.0293154601109]
(array([ 1.32753141,  0.02646156]), [[1.3005365921998688, 1.3545262368760884], [0.023607653
```



You can see by inspection that the fit looks pretty reasonable. The parameter confidence intervals are not too big, so we can be pretty confident of their values.

8.9 Nonlinear curve fitting with confidence intervals

Our goal is to fit this equation to data $y = c1exp(-x) + c2 * x$ and compute the confidence intervals on the parameters.

This is actually could be a linear regression problem, but it is convenient to illustrate the use the nonlinear fitting routine because it makes it easy to get confidence intervals for comparison. The basic idea is to use the covariance matrix returned from the nonlinear fitting routine to estimate the student-t corrected confidence interval.

```
# Nonlinear curve fit with confidence interval
import numpy as np
from scipy.optimize import curve_fit
from scipy.stats.distributions import  t

x = np.array([ 0.1,  0.2,  0.3,  0.4,  0.5,  0.6,  0.7,  0.8,  0.9,  1. ])
y = np.array([ 4.70192769,  4.46826356,  4.57021389,  4.29240134,  3.88155125,
               3.78382253,  3.65454727,  3.86379487,  4.16428541,  4.06079909])

# this is the function we want to fit to our data
def func(x,c0, c1):
    return c0 * np.exp(-x) + c1*x

pars, pcov = curve_fit(func, x, y, p0=[4.96, 2.11])

```

```
alpha = 0.05 # 95% confidence interval

n = len(y)    # number of data points
p = len(pars) # number of parameters

dof = max(0, n-p) # number of degrees of freedom

tval = t.ppf(1.0 - alpha / 2.0, dof) # student-t value for the dof and confidence level

for i, p,var in zip(range(n), pars, np.diag(pcov)):
    sigma = var**0.5
    print 'c{0}: {1} [{2}  {3}]'.format(i, p,
                                        p - sigma*tval,
                                        p + sigma*tval)

import matplotlib.pyplot as plt
plt.plot(x,y,'bo ')
xfit = np.linspace(0,1)
yfit = func(xfit, pars[0], pars[1])
plt.plot(xfit,yfit,'b-')
plt.legend(['data','fit'],loc='best')
plt.savefig('images/nonlin-fit-ci.png')
```

```
c0: 4.96713966439 [4.62674476567  5.30753456311]
c1: 2.10995112628 [1.76711622427  2.45278602828]
```

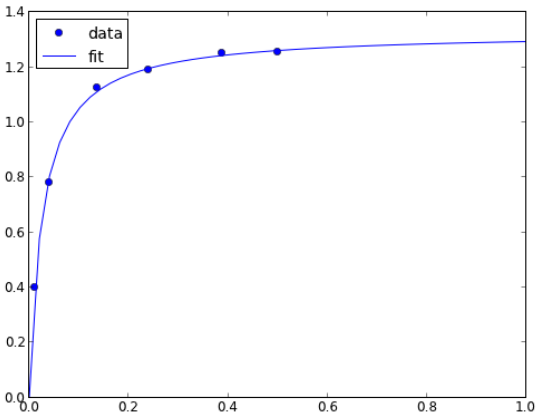


Figure 3: Nonlinear fit to data.

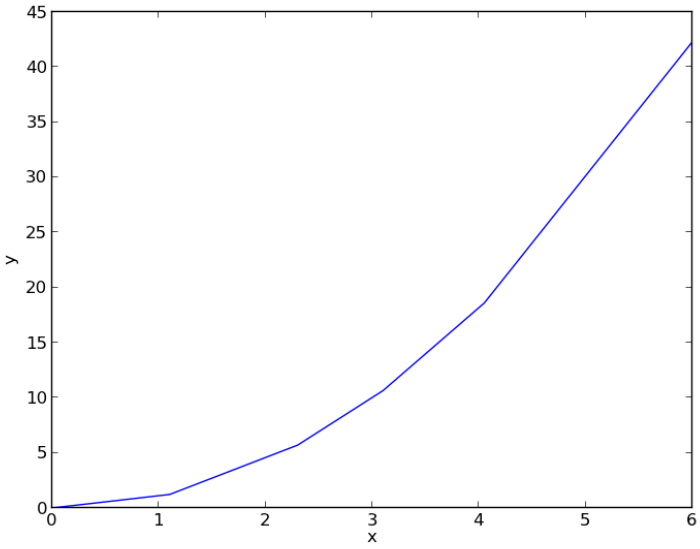
8.10 Parameter estimation by directly minimizing summed squared errors

Matlab post

```
import numpy as np
import matplotlib.pyplot as plt

```

```
x = np.array([0.0,      1.1,      2.3,      3.1,      4.05,     6.0])
y = np.array([0.0039,   1.2270,   5.7035,   10.6472,  18.6032,  42.3024])

plt.plot(x, y)
plt.xlabel('x')
plt.ylabel('y')
plt.savefig('images/nonlin-minsse-1.png')
```

```
>>> >>> >>> >>> >>> [<matplotlib.lines.Line2D object at 0x000000000733D898>]
<matplotlib.text.Text object at 0x00000000071EC5C0>
<matplotlib.text.Text object at 0x00000000071EED30>
```

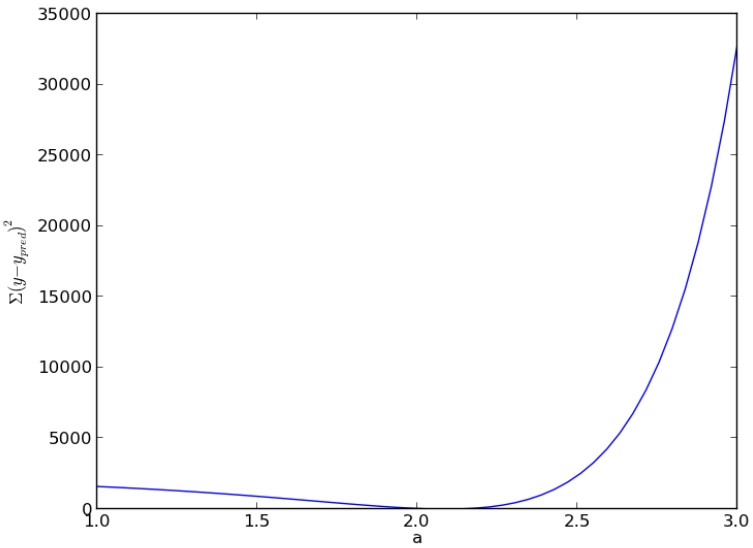


We are going to fit the function $y = x^a$ to the data. The best a will minimize the summed squared error between the model and the fit.

```
def errfunc_(a):
    return np.sum((y - x**a)**2)

errfunc = np.vectorize(errfunc_)

arange = np.linspace(1, 3)
sse = errfunc(arange)

plt.figure()
plt.plot(arange, sse)
plt.xlabel('a')
plt.ylabel('$\Sigma (y - y_{pred})^2$')
plt.savefig('images/nonlin-minsse-2.png')
```

```
... >>> >>> >>> >>> >>> >>> <matplotlib.figure.Figure object at 0x000000000736DBA8>
```

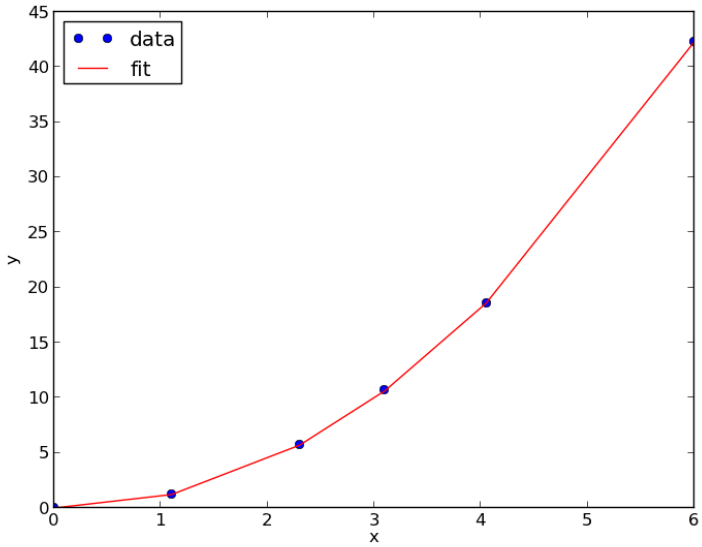
```
[<matplotlib.lines.Line2D object at 0x00000000075CBEF0>]
<matplotlib.text.Text object at 0x00000000076B8C18>
<matplotlib.text.Text object at 0x0000000007698BE0>
```



Based on the graph above, you can see a minimum in the summed squared error near $a = 2.1$. We use that as our initial guess. Since we know the answer is bounded, we use scipy.optimize.fminbound

```
from scipy.optimize import fminbound

amin = fminbound(errfunc, 1.0, 3.0)

print amin

plt.figure()
plt.plot(x, y, 'bo', label='data')
plt.plot(x, x**amin, 'r-', label='fit')
plt.xlabel('x')
plt.ylabel('y')
plt.legend(loc='best')
plt.savefig('images/nonlin-minsse-3.png')
```

```
>>> >>> >>> 2.09004838933
>>> <matplotlib.figure.Figure object at 0x00000000075D8470>
[<matplotlib.lines.Line2D object at 0x0000000007BDFA20>]
[<matplotlib.lines.Line2D object at 0x0000000007BDFC18>]
<matplotlib.text.Text object at 0x0000000007BC6828>
<matplotlib.text.Text object at 0x0000000007BCAF98>
<matplotlib.legend.Legend object at 0x0000000007BE3128>
```



We can do nonlinear fitting by directly minimizing the summed squared error between a model and data. This method lacks some of the features of other methods, notably the simple ability to get the confidence interval. However, this method is flexible and may offer more insight into how the solution depends on the parameters.

8.11 Reading in delimited text files

Matlab post

sometimes you will get data in a delimited text file format, .e.g. separated by commas or tabs. Matlab can read these in easily. Suppose we have a file containing this data:

```
1   3
3   4
5   6
4   8
```

It is easy to read this directly into variables like this:

```
1  import numpy as np
2
3  x,y = np.loadtxt('data/testdata.txt', unpack=True)
4
5  print x,y
```

```
[ 1.  3.  5.  4.] [ 3.  4.  6.  8.]
```

9 Interpolation

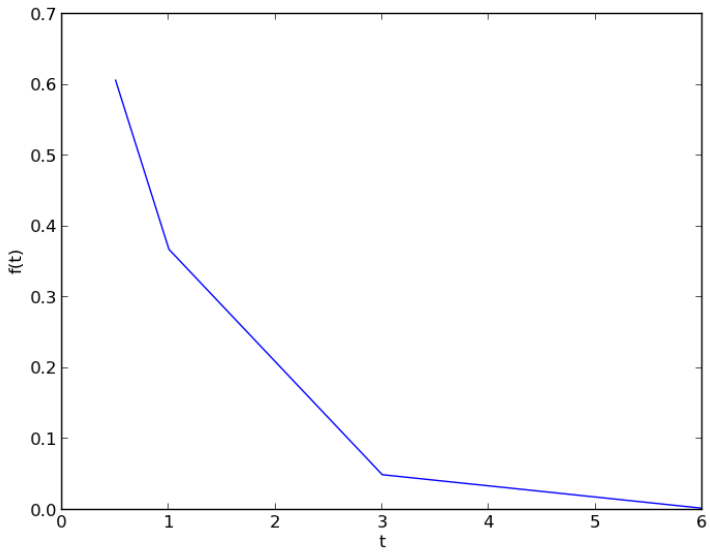
9.1 Better interpolate than never

Matlab post

We often have some data that we have obtained in the lab, and we want to solve some problem using the data. For example, suppose we have this data that describes the value of f at time t.

```
import matplotlib.pyplot as plt

t = [0.5, 1, 3, 6]
f = [0.6065,    0.3679,    0.0498,    0.0025]
plt.plot(t,f)
plt.xlabel('t')
plt.ylabel('f(t)')
plt.savefig('images/interpolate-1.png')
```

```
>>> >>> >>> [<matplotlib.lines.Line2D object at 0x04D18730>]
<matplotlib.text.Text object at 0x04BEE8B0>
<matplotlib.text.Text object at 0x04C03970>
```



9.1.1 Estimate the value of f at t=2.

This is a simple interpolation problem.

```
from scipy.interpolate import interp1d

```

```
g = interp1d(t, f) # default is linear interpolation

print g(2)
print g([2, 3, 4])
```

```
>>> >>> >>> 0.20885
[ 0.20885      0.0498       0.03403333]
```

The function we sample above is actually f(t) = exp(-t). The linearly interpolated example is not too accurate.

```
import numpy as np
print np.exp(-2)
```

```
0.135335283237
```

9.1.2 improved interpolation?

we can tell interp1d to use a different interpolation scheme such as cubic polynomial splines like this. For nonlinear functions, this may improve the accuracy of the interpolation, as it implicitly includes information about the curvature by fitting a cubic polynomial over neighboring points.

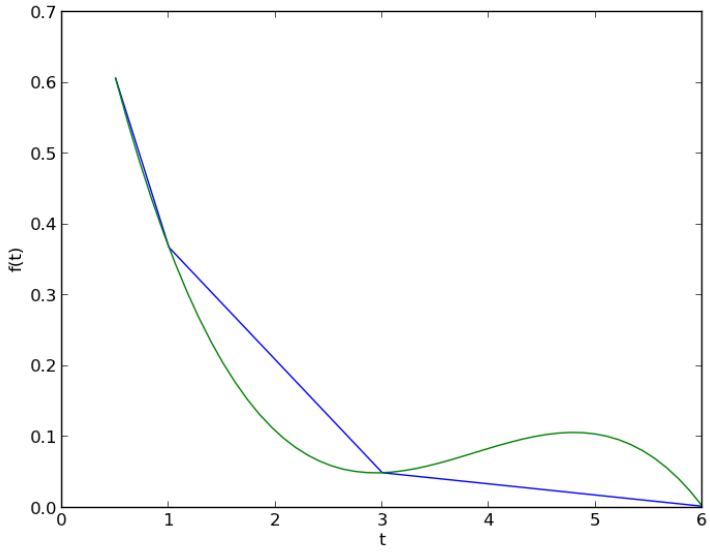
```
g2 = interp1d(t, f, 'cubic')
print g2(2)
print g2([2, 3, 4])
```

```
0.108481818182
[ 0.10848182  0.0498      0.08428727]
```

Interestingly, this is a different value than Matlab's cubic interpolation. Let us show the cubic spline fit.

```
plt.figure()
plt.plot(t,f)
plt.xlabel('t')
plt.ylabel('f(t)')

x = np.linspace(0.5, 6)
fit = g2(x)
plt.plot(x, fit, label='fit')
plt.savefig('images/interpolation-2.png')
```

```
<matplotlib.figure.Figure object at 0x04EF2430>
[<matplotlib.lines.Line2D object at 0x04F20ED0>]
<matplotlib.text.Text object at 0x04EF2FF0>
<matplotlib.text.Text object at 0x04F060D0>
>>> >>> >>> [<matplotlib.lines.Line2D object at 0x04F17570>]
```



Wow. That is a weird looking fit. Very different from what Matlab produces. This is a good teaching moment not to rely blindly on interpolation! We will rely on the linear interpolation from here out which behaves predictably.

9.1.3 The inverse question

It is easy to interpolate a new value of f given a value of t. What if we want to know the time that f=0.2? We can approach this a few ways.

- method 1
  We setup a function that we can use fsolve on. The function will be equal to zero at the time. The second function will look like 0 = 0.2 - f(t). The answer for 0.2=exp(-t) is t = 1.6094. Since we use interpolation here, we will get an approximate answer.

```
from scipy.optimize import fsolve

def func(t):
    return 0.2 - g(t)

initial_guess = 2
ans, = fsolve(func, initial_guess)
print ans
```

```
>>> ... ... >>> >>> >>> 2.0556428796
```

- method 2: switch the interpolation order
  We can switch the order of the interpolation to solve this problem. An

issue we have to address in this method is that the "x" values must be monotonically *increasing*. It is somewhat subtle to reverse a list in python. I will use the cryptic syntax of [::-1] instead of the list.reverse() function or reversed() function. list.reverse() actually reverses the list "in place", which changes the contents of the variable. That is not what I want. reversed() returns an iterator which is also not what I want. [::-1] is a fancy indexing trick that returns a reversed list.

```
g3 = interp1d(f[::-1], t[::-1])

print g3(0.2)
```

```
>>> 2.0556428796
```

9.1.4 A harder problem

Suppose we want to know at what time is 1/f = 100? Now we have to decide what do we interpolate: f(t) or 1/f(t). Let us look at both ways and decide what is best. The answer to $1/exp(-t) = 100$ is 4.6052

- interpolate on f(t) then invert the interpolated number

```
def func(t):
    'objective function. we do some error bounds because we cannot interpolate out of the range.'
    if t < 0.5: t=0.5
    if t > 6: t = 6
    return 100 - 1.0 / g(t)

initial_guess = 4.5
a1, = fsolve(func, initial_guess)
print a1
print 'The %error is {0:%}'.format((a1 - 4.6052)/4.6052)
```

```
... ... ... ... >>> >>> >>> 5.52431289641
The %error is 19.958154%
```

- invert f(t) then interpolate on 1/f

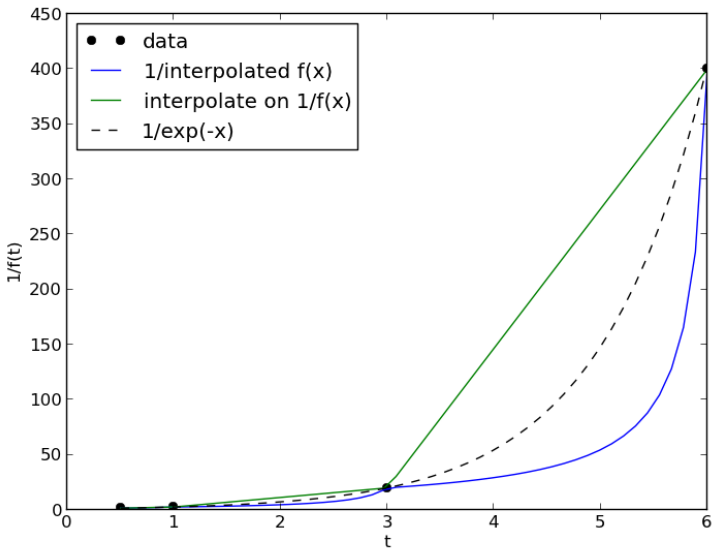
```
ig = interp1d(t, 1.0 / np.array(f))

def ifunc(t):
    if t < 0.5: t=0.5
    if t > 6: t = 6
    return 100 - ig(t)

initial_guess = 4.5
a2, = fsolve(ifunc, initial_guess)
print a2
print 'The %error is {0:%}'.format((a2 - 4.6052)/4.6052)
```

```
>>> ... ... ... ... >>> >>> >>> 3.6310782241
The %error is -21.152649%
```

9.1.5 Discussion

In this case you get different errors, one overestimates and one underestimates the answer, and by a lot: ± 20%. Let us look at what is happening.

```
1  import matplotlib.pyplot as plt
2  import numpy as np
3  from scipy.interpolate import interp1d
4
5  t = [0.5, 1, 3, 6]
6  f = [0.6065,    0.3679,    0.0498,    0.0025]
7
8  x = np.linspace(0.5, 6)
9
10
11 g = interp1d(t, f) # default is linear interpolation
12 ig = interp1d(t, 1.0 / np.array(f))
13
14 plt.figure()
15 plt.plot(t, 1 / np.array(f), 'ko ', label='data')
16 plt.plot(x, 1 / g(x), label='1/interpolated f(x)')
17 plt.plot(x, ig(x), label='interpolate on 1/f(x)')
18 plt.plot(x, 1 / np.exp(-x), 'k--', label='1/exp(-x)')
19 plt.xlabel('t')
20 plt.ylabel('1/f(t)')
21 plt.legend(loc='best')
22 plt.savefig('images/interpolation-3.png')
```



You can see that the 1/interpolated f(x) underestimates the value, while interpolated (1/f(x)) overestimates the value. This is an example of where

you clearly need more data in that range to make good estimates. Neither interpolation method is doing a great job. The trouble in reality is that you often do not know the real function to do this analysis. Here you can say the time is probably between 3.6 and 5.5 where 1/f(t) = 100, but you can not read much more than that into it. If you need a more precise answer, you need better data, or you need to use an approach other than interpolation. For example, you could fit an exponential function to the data and use that to estimate values at other times.

So which is the best to interpolate? I think you should interpolate the quantity that is linear in the problem you want to solve, so in this case I think interpolating 1/f(x) is better. When you use an interpolated function in a nonlinear function, strange, unintuitive things can happen. That is why the blue curve looks odd. Between data points are linear segments in the original interpolation, but when you invert them, you cause the curvature to form.

9.2 Interpolation of data

Matlab post

When we have data at two points but we need data in between them we use interpolation. Suppose we have the points (4,3) and (6,2) and we want to know the value of y at x=4.65, assuming y varies linearly between these points. we use the interp1d command to achieve this. The syntax in python is slightly different than in matlab.

```
from scipy.interpolate import interp1d

x = [4, 6]
y = [3, 2]

ifunc = interp1d(x, y)

print ifunc(4.65)


ifunc = interp1d(x, y, bounds_error=False) # do not raise error on out of bounds
print ifunc([4.65, 5.01, 4.2, 9])
```

```
2.675
[ 2.675  2.495  2.9      nan]
```

The default interpolation method is simple linear interpolation between points. Other methods exist too, such as fitting a cubic spline to the data and using the spline representation to interpolate from.

```
from scipy.interpolate import interp1d

x = [1, 2, 3, 4];
y = [1, 4, 9, 16]; # y = x^2

xi = [ 1.5, 2.5, 3.5]; # we want to interpolate on these values
y1 = interp1d(x,y)

```

```
print y1(xi)

y2 = interp1d(x,y,'cubic')
print y2(xi)

import numpy as np
print np.array(xi)**2
```

```
[  2.5   6.5  12.5]
[  2.25   6.25  12.25]
[  2.25   6.25  12.25]
```

In this case the cubic spline interpolation is more accurate than the linear interpolation. That is because the underlying data was polynomial in nature, and a spline is like a polynomial. That may not always be the case, and you need some engineering judgement to know which method is best.

9.3 Interpolation with splines

When you do not know the functional form of data to fit an equation, you can still fit/interpolate with splines.

```
# use splines to fit and interpolate data
from scipy.interpolate import interp1d
from scipy.optimize import fmin
import numpy as np
import matplotlib.pyplot as plt

x = np.array([ 0,      1,      2,      3,      4    ])
y = np.array([ 0.,     0.308,  0.55,   0.546,  0.44 ])

# create the interpolating function
f = interp1d(x, y, kind='cubic', bounds_error=False)

# to find the maximum, we minimize the negative of the function. We
# cannot just multiply f by -1, so we create a new function here.
f2 = interp1d(x, -y, kind='cubic')
xmax = fmin(f2, 2.5)

xfit = np.linspace(0,4)

plt.plot(x,y,'bo')
plt.plot(xfit, f(xfit),'r-')
plt.plot(xmax, f(xmax),'g*')
plt.legend(['data','fit','max'], loc='best', numpoints=1)
plt.xlabel('x data')
plt.ylabel('y data')
plt.title('Max point = ({0:1.2f}, {1:1.2f})'.format(float(xmax),
                                                    float(f(xmax))))
plt.savefig('images/splinefit.png')
```

```
Optimization terminated successfully.
         Current function value: -0.575712
         Iterations: 12
         Function evaluations: 24
```

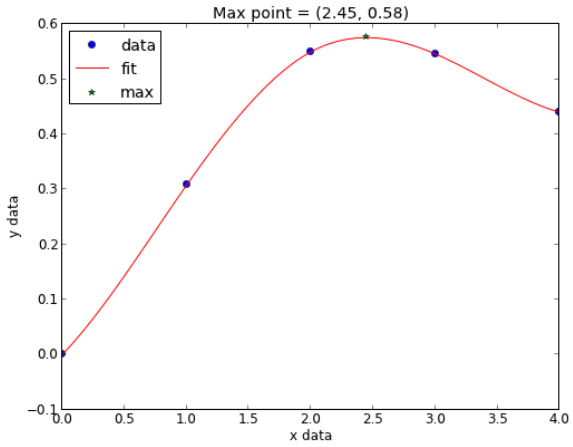


Figure 4: Illustration of a spline fit to data and finding the maximum point.

There are other good examples at http://docs.scipy.org/doc/scipy/reference/tutorial/interpolate.html

10 Optimization

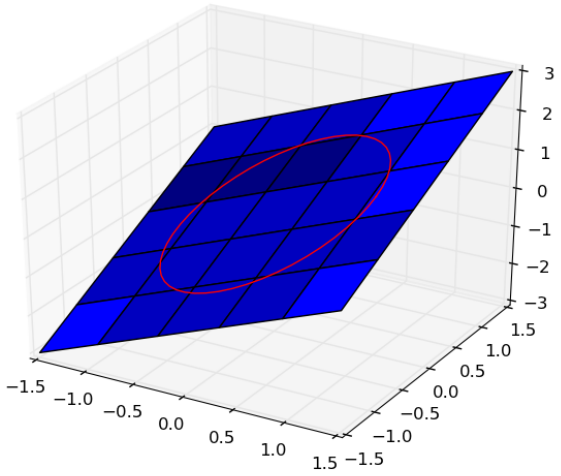
10.1 Using Lagrange multipliers in optimization

Matlab post (adapted from http://en.wikipedia.org/wiki/Lagrange_multipliers.)

Suppose we seek to maximize the function $f(x, y) = x + y$ subject to the constraint that $x^2 + y^2 = 1$. The function we seek to maximize is an unbounded plane, while the constraint is a unit circle. We want the maximum value of the circle, on the plane. We plot these two functions here.

```
1  import numpy as np
2
3  x = np.linspace(-1.5, 1.5)
4
5  [X, Y] = np.meshgrid(x, x)
6
7  import matplotlib as mpl
8  from mpl_toolkits.mplot3d import Axes3D
9  import matplotlib.pyplot as plt
10
11 fig = plt.figure()
12 ax = fig.gca(projection='3d')
13
14 ax.plot_surface(X, Y, X + Y)
15
16 theta = np.linspace(0,2*np.pi);
17 R = 1.0
18 x1 = R * np.cos(theta)
19 y1 = R * np.sin(theta)
20
```

```
21  ax.plot(x1, y1, x1 + y1, 'r-')
22  plt.savefig('images/lagrange-1.png')
```



10.1.1 Construct the Lagrange multiplier augmented function

To find the maximum, we construct the following function: $\Lambda(x, y; \lambda) = f(x, y) + \lambda g(x, y)$ where $g(x, y) = x^2 + y^2 - 1 = 0$, which is the constraint function. Since $g(x, y) = 0$, we are not really changing the original function, provided that the constraint is met!

```
1  import numpy as np
2
3  def func(X):
4      x = X[0]
5      y = X[1]
6      L = X[2] # this is the multiplier. lambda is a reserved keyword in python
7      return x + y + L * (x**2 + y**2 - 1)
```

10.1.2 Finding the partial derivatives

The minima/maxima of the augmented function are located where all of the partial derivatives of the augmented function are equal to zero, i.e. $\partial\Lambda/\partial x = 0$, $\partial\Lambda/\partial y = 0$, and $\partial\Lambda/\partial\lambda = 0$. the process for solving this is usually to analytically evaluate the partial derivatives, and then solve the unconstrained resulting equations, which may be nonlinear.

Rather than perform the analytical differentiation, here we develop a way to numerically approximate the partial derivatives.

```
def dfunc(X):
    dLambda = np.zeros(len(X))
    h = 1e-3 # this is the step size used in the finite difference.
    for i in range(len(X)):
        dX = np.zeros(len(X))
        dX[i] = h
        dLambda[i] = (func(X+dX)-func(X-dX))/(2*h);
    return dLambda
```

10.1.3 Now we solve for the zeros in the partial derivatives

The function we defined above (dfunc) will equal zero at a maximum or minimum. It turns out there are two solutions to this problem, but only one of them is the maximum value. Which solution you get depends on the initial guess provided to the solver. Here we have to use some judgement to identify the maximum.

```
from scipy.optimize import fsolve

# this is the max
X1 = fsolve(dfunc, [1, 1, 0])
print X1, func(X1)

# this is the min
X2 = fsolve(dfunc, [-1, -1, 0])
print X2, func(X2)
```

```
>>> ... >>> [ 0.70710678  0.70710678 -0.70710678] 1.41421356237
>>> ... >>> [-0.70710678 -0.70710678  0.70710678] -1.41421356237
```

10.1.4 Summary

Three dimensional plots in matplotlib are a little more difficult than in Matlab (where the code is almost the same as 2D plots, just different commands, e.g. plot vs plot3). In Matplotlib you have to import additional modules in the right order, and use the object oriented approach to plotting as shown here.

10.2 Constrained optimization

Matlab post

adapted from http://en.wikipedia.org/wiki/Lagrange_multipliers.

Suppose we seek to minimize the function $f(x, y) = x + y$ subject to the constraint that $x^2 + y^2 = 1$. The function we seek to maximize is an unbounded plane, while the constraint is a unit circle. We could setup a Lagrange multiplier approach to solving this problem, but we will use a constrained optimization approach instead.

```
from scipy.optimize import fmin_slsqp

def objective(X):
```

```
    x, y = X
    return x + y

def eqc(X):
    'equality constraint'
    x, y = X
    return x**2 + y**2 - 1.0

X0 = [-1, -1]
X = fmin_slsqp(objective, X0, eqcons=[eqc])
print X
```

```
Optimization terminated successfully.    (Exit mode 0)
            Current function value: -1.41421356237
            Iterations: 5
            Function evaluations: 20
            Gradient evaluations: 5
[-0.70710678 -0.70710678]
```

10.3 Linear programming example with inequality constraints

Matlab post

adapted from http://www.matrixlab-examples.com/linear-programming.html which solves this problem with fminsearch.

Let us suppose that a merry farmer has 75 roods (4 roods = 1 acre) on which to plant two crops: wheat and corn. To produce these crops, it costs the farmer (for seed, water, fertilizer, etc.) $120 per rood for the wheat, and $210 per rood for the corn. The farmer has $15,000 available for expenses, but after the harvest the farmer must store the crops while awaiting favorable or good market conditions. The farmer has storage space for 4,000 bushels. Each rood yields an average of 110 bushels of wheat or 30 bushels of corn. If the net profit per bushel of wheat (after all the expenses) is $1.30 and for corn is $2.00, how should the merry farmer plant the 75 roods to maximize profit?

Let x be the number of roods of wheat planted, and y be the number of roods of corn planted. The profit function is: $P = (110)(1.3)\mathrm{x} + (30)(2)y = 143x{+}60y$

There are some constraint inequalities, specified by the limits on expenses, storage and roodage. They are:

$\$120x + \$210y <= \$15000$ (The total amount spent cannot exceed the amount the farm has)

$110x + 30y <= 4000$ (The amount generated should not exceed storage space.)

$x + y <= 75$ (We cannot plant more space than we have.)

$0 <= xand0 <= y$ (all amounts of planted land must be positive.)

To solve this problem, we cast it as a linear programming problem, which minimizes a function f(X) subject to some constraints. We create a proxy function for the negative of profit, which we seek to minimize.

f = -(143*x + 60*y)

```
from scipy.optimize import fmin_cobyla

def objective(X):
    '''objective function to minimize. It is the negative of profit,
    which we seek to maximize.'''
    x, y = X
    return -(143*x + 60*y)

def c1(X):
    'Ensure 120x + 210y <= 15000'
    x,y = X
    return 15000 - 120 * x - 210*y

def c2(X):
    'ensure 110x + 30y <= 4000'
    x,y = X
    return 4000 - 110*x - 30 * y

def c3(X):
    'Ensure x + y is less than or equal to 75'
    x,y = X
    return 75 - x - y

def c4(X):
    'Ensure x >= 0'
    return X[0]

def c5(X):
    'Ensure y >= 0'
    return X[1]

X = fmin_cobyla(objective, x0=[20, 30], cons=[c1, c2, c3, c4, c5])

print 'We should plant {0:1.2f} roods of wheat.'.format(X[0])
print 'We should plant {0:1.2f} roods of corn'.format(X[1])
print 'The maximum profit we can earn is ${0:1.2f}.'.format(-objective(X))
```

```
    Normal return from subroutine COBYLA

    NFVALS =   40   F =-6.315625E+03    MAXCV = 4.547474E-13
    X = 2.187500E+01   5.312500E+01
We should plant 21.88 roods of wheat.
We should plant 53.12 roods of corn
The maximum profit we can earn is $6315.62.
```

This code is not exactly the same as the original post, but we get to the same answer. The linear programming capability in scipy is currently somewhat limited in 0.10. It is a little better in 0.11, but probably not as advanced as Matlab. There are some external libraries available:

1. http://abel.ee.ucla.edu/cvxopt/
2. http://openopt.org/LP

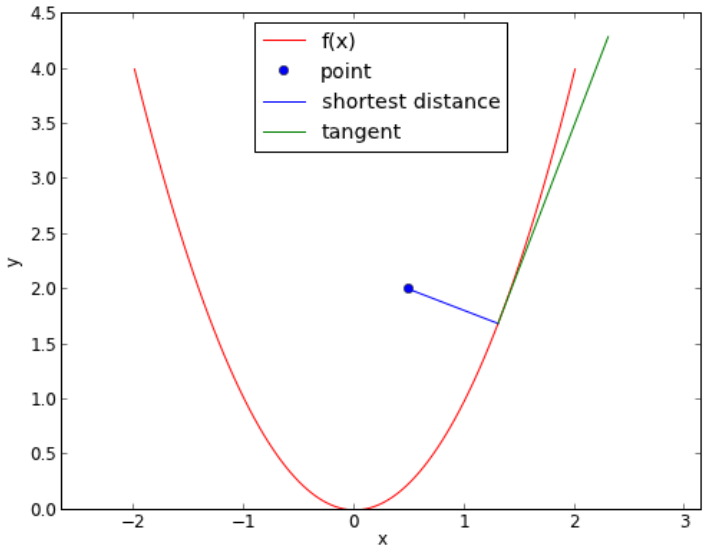
10.4 Find the minimum distance from a point to a curve.

A problem that can be cast as a constrained minimization problem is to find the minimum distance from a point to a curve. Suppose we have $f(x) = x^2$,

and the point (0.5, 2). what is the minimum distance from that point to $f(x)$?

```
import numpy as np
import matplotlib.pyplot as plt
from scipy.optimize import fmin_cobyla

P = (0.5, 2)

def f(x):
    return x**2

def objective(X):
    x,y = X
    return np.sqrt((x - P[0])**2 + (y - P[1])**2)

def c1(X):
    x,y = X
    return f(x) - y

X = fmin_cobyla(objective, x0=[0.5,0.5], cons=[c1])

print 'The minimum distance is {0:1.2f}'.format(objective(X))

# Verify the vector to this point is normal to the tangent of the curve
# position vector from curve to point
v1 = np.array(P) - np.array(X)
# position vector
v2 = np.array([1, 2.0 * X[0]])
print 'dot(v1, v2) = ',np.dot(v1, v2)

x = np.linspace(-2, 2, 100)

plt.plot(x, f(x), 'r-', label='f(x)')
plt.plot(P[0], P[1], 'bo', label='point')
plt.plot([P[0], X[0]], [P[1], X[1]], 'b-', label='shortest distance')
plt.plot([X[0], X[0] + 1], [X[1], X[1] + 2.0 * X[0]], 'g-', label='tangent')
plt.axis('equal')
plt.xlabel('x')
plt.ylabel('y')
plt.legend(loc='best')
plt.savefig('images/min-dist-p-func.png')
```

```
The minimum distance is 0.86
dot(v1, v2) =  0.000336477214214

   Normal return from subroutine COBYLA

   NFVALS =   44   F = 8.579598E-01    MAXCV = 0.000000E+00
   X = 1.300793E+00   1.692061E+00
```



In the code above, we demonstrate that the point we find on the curve that minimizes the distance satisfies the property that a vector from that point to our other point is normal to the tangent of the curve at that point. This is shown by the fact that the dot product of the two vectors is very close to zero. It is not zero because of the accuracy criteria that is used to stop the minimization is not high enough.

11 Plotting

11.1 http://matlab.cheme.cmu.edu/2011/12/15/interacting-with-graphs-with-context-menus/

11.2 http://matlab.cheme.cmu.edu/2011/11/22/interacting-with-your-graph-through-mouse-clicks/

11.3 http://matlab.cheme.cmu.edu/2011/11/21/interacting-with-the-steam-entropy-temperature-chart/

11.4 http://matlab.cheme.cmu.edu/2011/12/07/interacting-with-graphs-with-keypresses/

11.5 http://matlab.cheme.cmu.edu/2011/11/24/turkeyfy-your-plots/

11.6 http://matlab.cheme.cmu.edu/2011/11/22/3d-plots-of-the-steam-tables/

11.7 http://matlab.cheme.cmu.edu/2011/11/11/interacting-with-labeled-data-points/

11.8 http://matlab.cheme.cmu.edu/2011/09/13/check-out-the-new-fall-colors/

11.9 http://matlab.cheme.cmu.edu/2011/09/14/picassos-short-lived-blue-period-with-matlab/

11.10 http://matlab.cheme.cmu.edu/2011/09/16/customizing-plots-after-the-fact/

11.11 http://matlab.cheme.cmu.edu/2011/08/25/plotting-two-datasets-with-very-different-scales/

11.12 http://matlab.cheme.cmu.edu/2011/08/01/basic-plotting-tutorial/

11.13 http://matlab.cheme.cmu.edu/2011/08/01/plot-customizations-modifying-line-text-and-figure-properties/

12 Programming

12.1 Some of this, sum of that

Matlab plot

Python provides a sum function to compute the sum of a list. However, the sum function does not work on every arrangement of numbers, and it certainly does not work on nested lists. We will solve this problem with recursion.

Here is a simple example.

```
v = [1, 2, 3, 4, 5, 6, 7, 8, 9] # a list
print sum(v)

v = (1, 2, 3, 4, 5, 6, 7, 8, 9)  # a tuple
print sum(v)
```

```
45
45
```

If you have data in a dictionary, sum works by default on the keys. You can give the sum function the values like this.

```
v = {'a':1, 'b':3, 'c':4}
print sum(v.values())
```

```
8
```

12.1.1 Nested lists

Suppose now we have nested lists. This kind of structured data might come up if you had grouped several things together. For example, suppose we have 5 departments, with 1, 5, 15, 7 and 17 people in them, and in each department they are divided into groups.

Department 1: 1 person Department 2: group of 2 and group of 3 Department 3: group of 4 and 11, with a subgroups of 5 and 6 making up the group of 11. Department 4: 7 people Department 5: one group of 8 and one group of 9.

We might represent the data like this nested list. Now, if we want to compute the total number of people, we need to add up each group. We cannot simply sum the list, because some elements are single numbers, and others are lists, or lists of lists. We need to recurse through each entry until we get down to a number, which we can add to the running sum.

```
v = [1,
     [2, 3],
     [4, [5, 6]],
     7,
     [8,9]]

def recursive_sum(X):
    'compute sum of arbitrarily nested lists'
    s = 0 # initial value of the sum

    for i in range(len(X)):
        import types  # we use this to test if we got a number
        if isinstance(X[i], (types.IntType,
                             types.LongType,
                             types.FloatType,
```

```
                                types.ComplexType)):
            # this is the terminal step
            s += X[i]
        else:
            # we did not get a number, so we recurse
            s += recursive_sum(X[i])
    return s

print recursive_sum(v)
print recursive_sum([1,2,3,4,5,6,7,8,9]) # test on non-nested list
```

```
45
45
```

In Post 1970 we examined recursive functions that could be replaced by loops. Here we examine a function that can only work with recursion because the nature of the nested data structure is arbitrary. There are arbitary branches and depth in the data structure. Recursion is nice because you do not have to define that structure in advance.

12.2 Lather, rinse and repeat

Matlab post

Recursive functions are functions that call themselves repeatedly until some exit condition is met. Today we look at a classic example of recursive function for computing a factorial. The factorial of a non-negative integer n is denoted n!, and is defined as the product of all positive integers less than or equal to n.

The key ideas in defining a recursive function is that there needs to be some logic to identify when to terminate the function. Then, you need logic that calls the function again, but with a smaller part of the problem. Here we recursively call the function with n-1 until it gets called with n=0. 0! is defined to be 1.

```
def recursive_factorial(n):
    '''compute the factorial recursively. Note if you put a negative
    number in, this function will never end. We also do not check if
    n is an integer.'''
    if n == 0:
        return 1
    else:
        return n * recursive_factorial(n - 1)

print recursive_factorial(5)
```

```
120
```

```
from scipy.misc import factorial
print factorial(5)
```

```
120.0
```

12.2.1 Conclusions

Recursive functions have a special niche in mathematical programming. There is often another way to accomplish the same goal. That is not always true though, and in a future post we will examine cases where recursion is the only way to solve a problem.

12.3 regular expressions

http://matlab.cheme.cmu.edu/2012/05/07/1701/

12.4 Unique entries in a vector

Matlab post

It is surprising how often you need to know only the unique entries in a vector of entries. In python, we create a "set" from a list, which only contains unique entries. Then we convert the set back to a list.

```
a = [1, 1, 2, 3, 4, 5, 3, 5]

b = list(set(a))
print b
```

```
[1, 2, 3, 4, 5]
```

```
a = ['a',
     'b',
     'abracadabra',
     'b',
     'c',
     'd',
     'b']

print list(set(a))
```

```
['a', 'c', 'b', 'abracadabra', 'd']
```

12.5 Sorting in python

Matlab post

Occasionally it is important to have sorted data. Python has a few sorting options.

```
a = [4, 5, 1, 6, 8, 3, 2]
print a
a.sort()  # inplace sorting
print a

a.sort(reverse=True)
print a
```

```
[4, 5, 1, 6, 8, 3, 2]
[1, 2, 3, 4, 5, 6, 8]
[8, 6, 5, 4, 3, 2, 1]
```

If you do not want to modify your list, but rather get a copy of a sorted list, use the sorted command.

```
a = [4, 5, 1, 6, 8, 3, 2]
print 'sorted a = ',sorted(a)  # no change to a
print 'sorted a = ',sorted(a, reverse=True)  # no change to a
print 'a        = ',a
```

```
sorted a =  [1, 2, 3, 4, 5, 6, 8]
sorted a =  [8, 6, 5, 4, 3, 2, 1]
a        =  [4, 5, 1, 6, 8, 3, 2]
```

This works for strings too:

```
a = ['b', 'a', 'c', 'tree']
print sorted(a)
```

```
['a', 'b', 'c', 'tree']
```

Here is a subtle point though. A capitalized letter comes before a lowercase letter. We can pass a function to the sorted command that is called on each element prior to the sort. Here we make each word lower case before sorting.

```
a = ['B', 'a', 'c', 'tree']
print sorted(a)

# sort by lower case letter
print sorted(a, key=str.lower)
```

```
['B', 'a', 'c', 'tree']
['a', 'B', 'c', 'tree']
```

Here is a more complex sorting problem. We have a list of tuples with group names and the letter grade. We want to sort the list by the letter grades. We do this by creating a function that maps the letter grades to the position of the letter grades in a sorted list. We use the list.index function to find the index of the letter grade, and then sort on that.

```
groups = [('group1', 'B'),
          ('group2', 'A+'),
          ('group3', 'A')]

def grade_key(gtup):
    '''gtup is a tuple of ('groupname', 'lettergrade')'''
    lettergrade = gtup[1]

    grades = ['A++', 'A+', 'A', 'A-', 'A/B'
```

```
10                'B+', 'B', 'B-', 'B/C',
11                'C+', 'C', 'C-', 'C/D',
12                'D+', 'D', 'D-', 'D/R',
13                'R+', 'R', 'R-', 'R--']
14
15      return grades.index(lettergrade)
16
17  print sorted(groups, key=grade_key)
```

```
[('group2', 'A+'), ('group3', 'A'), ('group1', 'B')]
```

12.6 http://matlab.cheme.cmu.edu/2011/10/23/using-java-inside-matlab/

12.7 http://matlab.cheme.cmu.edu/2011/10/22/create-a-word-document-from-matlab/

12.8 http://matlab.cheme.cmu.edu/2011/08/07/manipulating-excel-with-matlab/

12.9 http://matlab.cheme.cmu.edu/2011/08/04/introduction-to-debugging-in-matlab/

13 Worked examples

13.1 Peak finding in Raman spectroscopy

Raman spectroscopy is a vibrational spectroscopy. The data typically comes as intensity vs. wavenumber, and it is discrete. Sometimes it is necessary to identify the precise location of a peak. In this post, we will use spline smoothing to construct an interpolating function of the data, and then use fminbnd to identify peak positions.

This example was originally worked out in Matlab at http://matlab.cheme.cmu.edu/2012/08/27/peak-finding-in-raman-spectroscopy/

numpy:loadtxt

Let us take a look at the raw data.

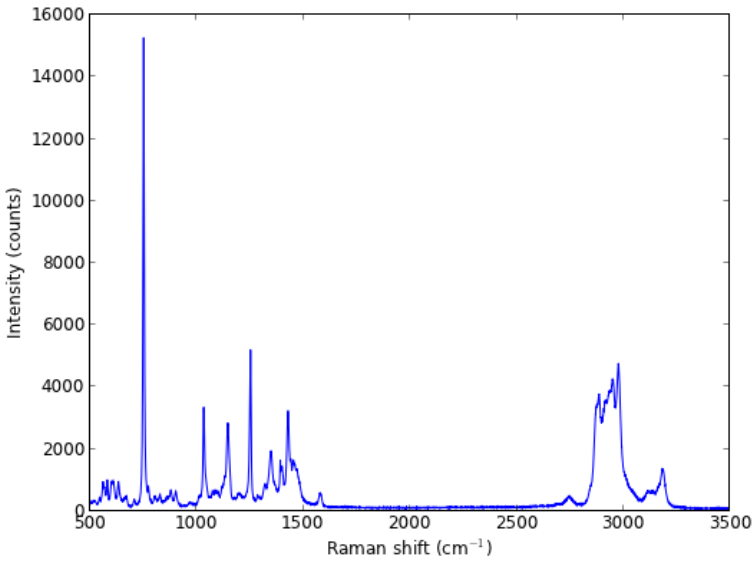
```
1  import os
2  print os.getcwd()
3  print os.environ['HOME']
```

```
/home/jkitchin/Dropbox/intro-python
/home/jkitchin
```

```
1  import numpy as np
2  import matplotlib.pyplot as plt
3
4  w, i = np.loadtxt('data/raman.txt', usecols=(0, 1), unpack=True)
5
```

```
plt.plot(w, i)
plt.xlabel('Raman shift (cm$^{-1}$)')
plt.ylabel('Intensity (counts)')
plt.savefig('images/raman-1.png')
plt.show()
```

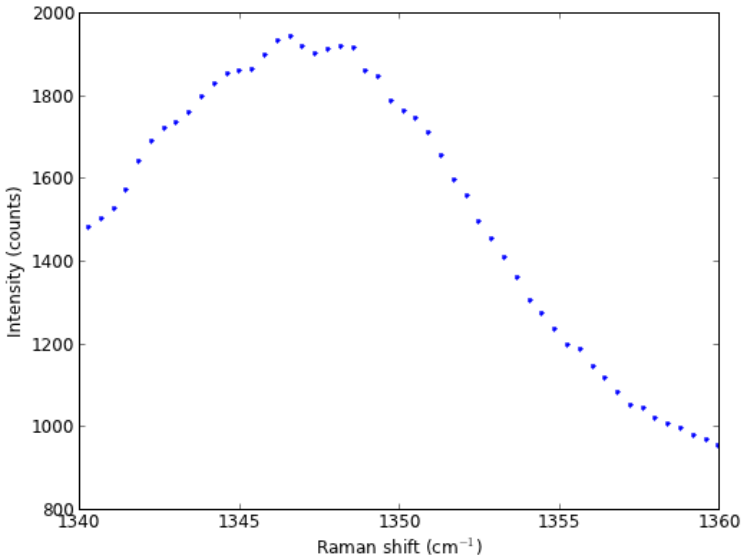
```
>>> >>> >>> >>> [<matplotlib.lines.Line2D object at 0x1d372810>]
<matplotlib.text.Text object at 0x1d48df90>
<matplotlib.text.Text object at 0x1d356a10>
```



The next thing to do is narrow our focus to the region we are interested in between 1340 cm^-1 and 1360 cm^-1.

```
ind = (w > 1340) & (w < 1360)
w1 = w[ind]
i1 = i[ind]

plt.plot(w1, i1, 'b. ')
plt.xlabel('Raman shift (cm$^{-1}$)')
plt.ylabel('Intensity (counts)')
plt.savefig('images/raman-2.png')
plt.show()
```

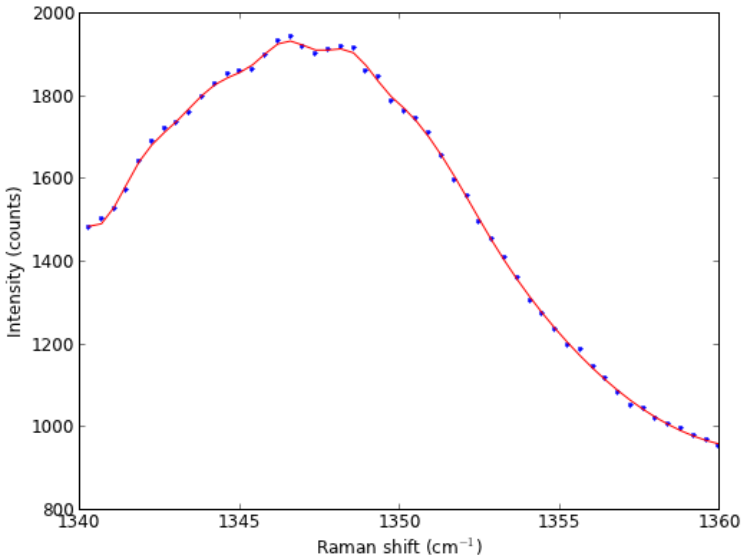
```
>>> [<matplotlib.lines.Line2D object at 0x1d5005d0>]
<matplotlib.text.Text object at 0x1d37a650>
<matplotlib.text.Text object at 0x1d3809d0>
```



Next we consider a scipy:UnivariateSpline. This function "smooths" the data.

```
from scipy.interpolate import UnivariateSpline

# s is a "smoothing" factor
sp = UnivariateSpline(w1, i1, s=3000)

plt.plot(w1, i1, 'b. ')
plt.plot(w1, sp(w1), 'r-')
plt.xlabel('Raman shift (cm$^{-1}$)')
plt.ylabel('Intensity (counts)')
plt.savefig('images/raman-3.png')
plt.show()
```

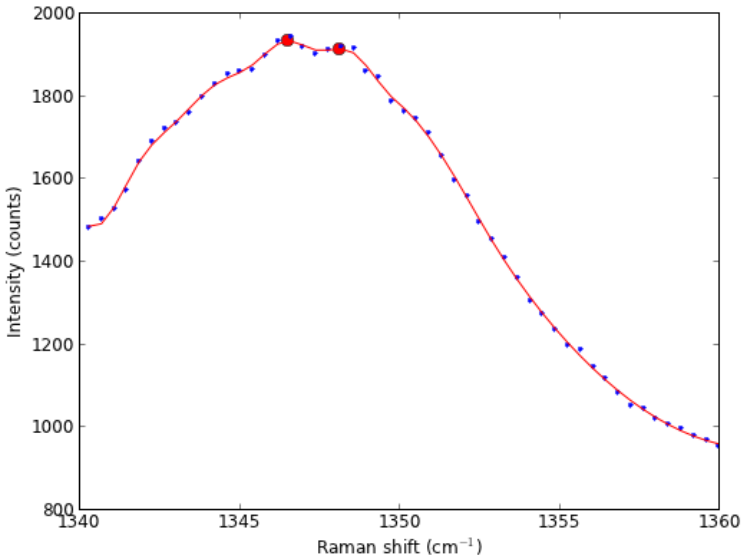
```
... [<matplotlib.lines.Line2D object at 0x1dd35e90>]
[<matplotlib.lines.Line2D object at 0x2ab334a3d510>]
<matplotlib.text.Text object at 0x1d49bad0>
<matplotlib.text.Text object at 0x1dd3b950>
```



Note that the UnivariateSpline function returns a "callable" function! Our next goal is to find the places where there are peaks. This is defined by the first derivative of the data being equal to zero. It is easy to get the first derivative of a UnivariateSpline with a second argument as shown below.

```
# get the first derivative evaluated at all the points
d1 =  sp(w1, 1)
plt.plot(w1, d1, label='first derivative')
plt.xlabel('Raman shift (cm$^{-1}$)')
plt.ylabel('First derivative')

# find the places where the first derivative crosses zero
s = np.zeros(d1.shape)
s[d1 >= 0] = 1
s[d1 < 0] = 0

initial_guesses = w1[np.diff(s) == -1]
plt.plot(initial_guesses, 0*initial_guesses, 'ro ', label='Guesses of zeros')
plt.legend(loc='best')
plt.savefig('images/raman-4.png'
plt.show()
```

```
>>> [<matplotlib.lines.Line2D object at 0x1d9eaad0>]
<matplotlib.text.Text object at 0x1d4f2210>
<matplotlib.text.Text object at 0x1d9e6910>
>>> ... >>> >>> >>> >>> >>> [<matplotlib.lines.Line2D object at 0x1d4f3250>]
<matplotlib.legend.Legend object at 0x1d839510>
```



Now, we can use these initial guesses to solve for the actual values.

```
from scipy.optimize import fminbound

def func(w):
    'function to minimize'
    return -sp(w)

for value in initial_guesses:
    sol = fminbound(func, value - 1, value + 1)
    plt.plot(sol, sp(sol), 'ro ', ms=8)
    print 'Peak found at {0} cm^{{-1}}'.format(sol)

plt.plot(w1, i1, 'b. ')
plt.plot(w1, sp(w1), 'r-')
plt.xlabel('Raman shift (cm$^{-1}$)')
plt.ylabel('Intensity (counts)')
plt.savefig('images/raman-5.png')
plt.show()
```

```
... ... ... >>> ... [<matplotlib.lines.Line2D object at 0x1da00510>]
Peak found at 1346.50980295 cm^{-1}
[<matplotlib.lines.Line2D object at 0x1d4c0110>]
Peak found at 1348.11261373 cm^{-1}
[<matplotlib.lines.Line2D object at 0x1da02b90>]
[<matplotlib.lines.Line2D object at 0x1da02750>]
<matplotlib.text.Text object at 0x1da01850>
<matplotlib.text.Text object at 0x1d9d4110>
```

In the end, we have illustrated how to construct a spline smoothing interpolation function and to find maxima in the function, including generating some

initial guesses. There is more art to this than you might like, since you have to judge how much smoothing is enough or too much. With too much, you may smooth peaks out. With too little, noise may be mistaken for peaks.

13.1.1 Summary notes

Using org-mode with :session allows a large script to be broken up into mini sections. However, it only seems to work with the default python mode in Emacs, and it does not work with emacs-for-python or the latest python-mode. I also do not really like the output style, e.g. the output from the plotting commands.

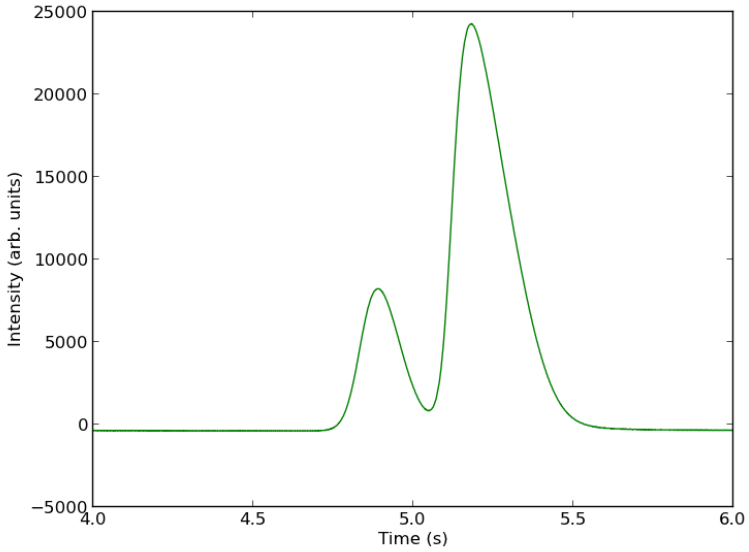
13.2 Curve fitting to get overlapping peak areas

Today we examine an approach to fitting curves to overlapping peaks to deconvolute them so we can estimate the area under each curve. We have a text file that contains data from a gas chromatograph with two peaks that overlap. We want the area under each peak to estimate the gas composition. You will see how to read the text file in, parse it to get the data for plotting and analysis, and then how to fit it.

A line like "# of Points 9969" tells us the number of points we have to read. The data starts after a line containing "R.Time Intensity". Here we read the number of points, and then get the data into arrays.

```
import numpy as np
import matplotlib.pyplot as plt

datafile = 'data/gc-data-21.txt'

i = 0
with open(datafile) as f:
    lines = f.readlines()

for i,line in enumerate(lines):
    if '# of Points' in line:
        npoints = int(line.split()[-1])
    elif 'R.Time        Intensity' in line:
        i += 1
        break

# now get the data
t, intensity = [], []
for j in range(i, i + npoints):
    fields = lines[j].split()
    t += [float(fields[0])]
    intensity += [int(fields[1])]

t = np.array(t)
intensity = np.array(intensity)

# now plot the data in the relevant time frame
plt.plot(t, intensity)
plt.xlim([4, 6])
plt.xlabel('Time (s)')
plt.ylabel('Intensity (arb. units)')
plt.savefig('images/deconvolute-1.png')
```

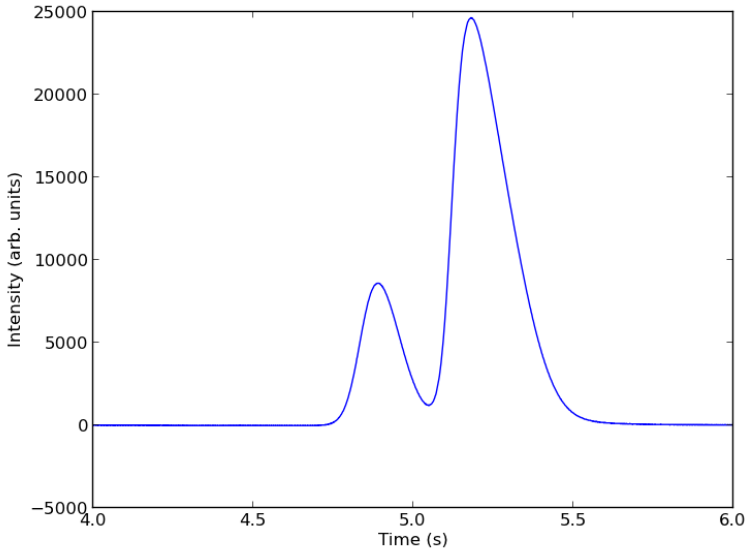
```
>>> >>> >>> >>> >>> ... ... >>> ... ... ... ... ... ... >>> ... >>> ... ... ... ... >>> >>>
(4, 6)
<matplotlib.text.Text object at 0x04BBB950>
<matplotlib.text.Text object at 0x04BD0A10>
```



You can see there is a non-zero baseline. We will normalize that by the average between 4 and 4.4 seconds.

```
1  intensity -= np.mean(intensity[(t> 4) & (t < 4.4)])
2  plt.figure()
3  plt.plot(t, intensity)
4  plt.xlim([4, 6])
5  plt.xlabel('Time (s)')
6  plt.ylabel('Intensity (arb. units)')
7  plt.savefig('./images/deconvolute-2.png')
```

```
<matplotlib.figure.Figure object at 0x04CF7950>
[<matplotlib.lines.Line2D object at 0x04DF5C30>]
(4, 6)
<matplotlib.text.Text object at 0x04DDB690>
<matplotlib.text.Text object at 0x04DE3630>
```



The peaks are asymmetric, decaying gaussian functions. We define a function for this

```
from scipy.special import erf

def asym_peak(t, pars):
    'from Anal. Chem. 1994, 66, 1294-1301'
    a0 = pars[0]  # peak area
    a1 = pars[1]  # elution time
    a2 = pars[2]  # width of gaussian
    a3 = pars[3]  # exponential damping term
    f = (a0/2/a3*np.exp(a2**2/2.0/a3**2 + (a1 - t)/a3)
         *(erf((t-a1)/(np.sqrt(2.0)*a2) - a2/np.sqrt(2.0)/a3) + 1.0))
    return f
```

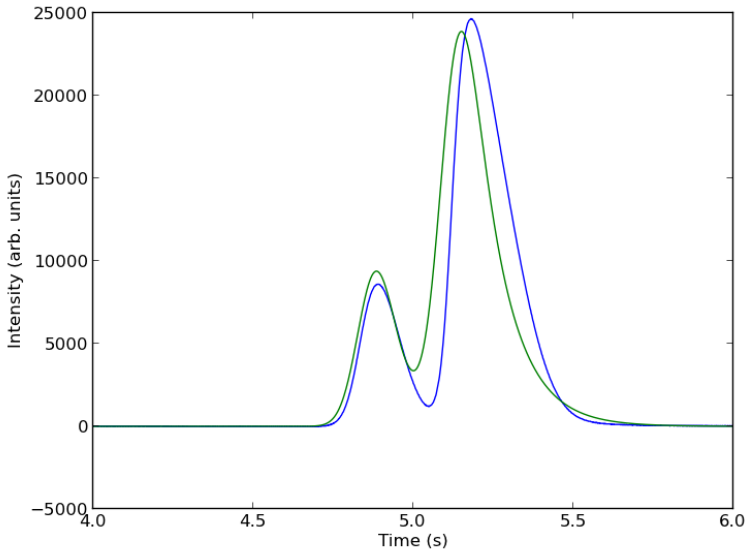
To get two peaks, we simply add two peaks together.

```
def two_peaks(t, *pars):
    'function of two overlapping peaks'
    a10 = pars[0]  # peak area
    a11 = pars[1]  # elution time
    a12 = pars[2]  # width of gaussian
    a13 = pars[3]  # exponential damping term
    a20 = pars[4]  # peak area
    a21 = pars[5]  # elution time
    a22 = pars[6]  # width of gaussian
    a23 = pars[7]  # exponential damping term
    p1 = asym_peak(t, [a10, a11, a12, a13])
    p2 = asym_peak(t, [a20, a21, a22, a23])
    return p1 + p2
```

To show the function is close to reasonable, we plot the fitting function with an initial guess for each parameter. The fit is not good, but we have only guessed the parameters for now.

```
parguess = (1500, 4.85, 0.05, 0.05, 5000, 5.1, 0.05, 0.1)
plt.figure()
plt.plot(t, intensity)
plt.plot(t,two_peaks(t, *parguess),'g-')
plt.xlim([4, 6])
plt.xlabel('Time (s)')
plt.ylabel('Intensity (arb. units)')
plt.savefig('images/deconvolution-3.png')
```

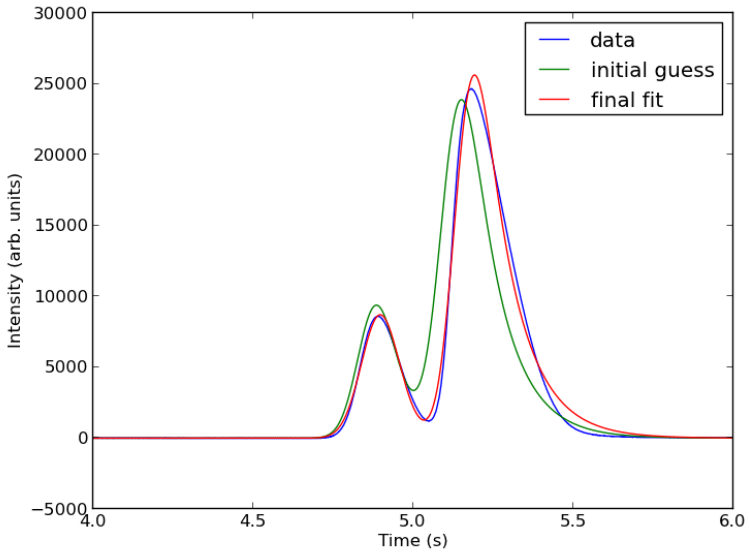
```
<matplotlib.figure.Figure object at 0x04FEF690>
[<matplotlib.lines.Line2D object at 0x05049870>]
[<matplotlib.lines.Line2D object at 0x04FEFA90>]
(4, 6)
<matplotlib.text.Text object at 0x0502E210>
<matplotlib.text.Text object at 0x050362B0>
```



Next, we use nonlinear curve fitting from scipy.optimize.curve_fit

```
from scipy.optimize import curve_fit

popt, pcov = curve_fit(two_peaks, t, intensity, parguess)
print popt

plt.plot(t, two_peaks(t, *popt), 'r-')
plt.legend(['data', 'initial guess','final fit'])

plt.savefig('images/deconvolution-4.png')
```

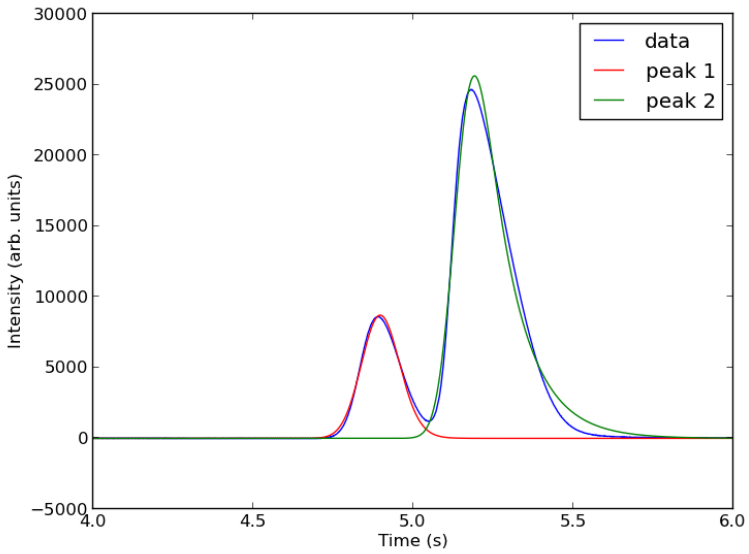
```
>>> >>> [  1.31039283e+03   4.87474330e+00   5.55414785e-02   2.50610175e-02
   5.32556821e+03   5.14121507e+00   4.68236129e-02   1.04105615e-01]
>>> [<matplotlib.lines.Line2D object at 0x0505BA10>]
<matplotlib.legend.Legend object at 0x05286270>
```



The fits are not perfect. The small peak is pretty good, but there is an unphysical tail on the larger peak, and a small mismatch at the peak. There is not much to do about that, it means the model peak we are using is not a good model for the peak. We will still integrate the areas though.

```
pars1 = popt[0:4]
pars2 = popt[4:8]

peak1 = asym_peak(t, pars1)
peak2 = asym_peak(t, pars2)

area1 = np.trapz(peak1, t)
area2 = np.trapz(peak2, t)

print 'Area 1 = {0:1.2f}'.format(area1)
print 'Area 2 = {0:1.2f}'.format(area2)

print 'Area 1 is {0:1.2%} of the whole area'.format(area1/(area1 + area2))
print 'Area 2 is {0:1.2%} of the whole area'.format(area2/(area1 + area2))

plt.figure()
plt.plot(t, intensity)
plt.plot(t, peak1, 'r-')
plt.plot(t, peak2, 'g-')
plt.xlim([4, 6])
plt.xlabel('Time (s)')
plt.ylabel('Intensity (arb. units)')
plt.legend(['data', 'peak 1', 'peak 2'])
plt.savefig('images/deconvolution-5.png')
```

```
>>> >>> >>> >>> >>> >>> >>> >>> Area 1 = 1310.39
Area 2 = 5325.57
>>> Area 1 is 19.75% of the whole area
Area 2 is 80.25% of the whole area
>>> <matplotlib.figure.Figure object at 0x05286ED0>
[<matplotlib.lines.Line2D object at 0x053A5AB0>]
[<matplotlib.lines.Line2D object at 0x05291D30>]
[<matplotlib.lines.Line2D object at 0x053B9810>]
(4, 6)
<matplotlib.text.Text object at 0x0529C4B0>
<matplotlib.text.Text object at 0x052A3450>
<matplotlib.legend.Legend object at 0x053B9ED0>
```



This sample was air, and the first peak is oxygen, and the second peak is nitrogen. we come pretty close to the actual composition of air, although it is low on the oxygen content. To do better, one would have to use a calibration curve.

In the end, the overlap of the peaks is pretty small, but it is still difficult to reliably and reproducibly deconvolute them. By using an algorithm like we have demonstrated here, it is possible at least to make the deconvolution reproducible.

13.2.1 Notable differences from Matlab

1. The order of arguments to np.trapz is reversed.

2. The order of arguments to the fitting function scipy.optimize.curve_fit is different than in Matlab.

3. The scipy.optimize.curve_fit function expects a fitting function that has all parameters as arguments, where Matlab expects a vector of parameters.

13.3 Estimating the boiling point of water

Matlab post

I got distracted looking for Shomate parameters for ethane today, and came across this website on predicting the boiling point of water using the Shomate equations. The basic idea is to find the temperature where the Gibbs energy of water as a vapor is equal to the Gibbs energy of the liquid.

```
import matplotlib.pyplot as plt
```

Liquid water ([[http://webbook.nist.gov/cgi/cbook.cgi?ID=C7732185&Units=SI&Mask=2#Thermo-Condensed][http://webbook.nist.gov/cgi/cbook.cgi?ID=C7732185&Units=SI&Mask=2#Thermo-Condensed]])

```
# valid over 298-500

Hf_liq = -285.830   # kJ/mol
S_liq = 0.06995     # kJ/mol/K
shomateL = [-203.6060,
             1523.290,
            -3196.413,
             2474.455,
                3.855326,
             -256.5478,
             -488.7163,
             -285.8304]
```

Gas phase water ([[http://webbook.nist.gov/cgi/cbook.cgi?ID=C7732185&Units=SI&Mask=1&Type=JANAFG&Table=on#JANAFG][http://webbook.nist.gov/cgi/cbook.cgi?ID=C7732185&Units=SI&Mask=1&Type=JANAFG&Table=on#JANAFG]])

Interestingly, these parameters are listed as valid only above 500K. That means we have to extrapolate the values down to 298K. That is risky for polynomial models, as they can deviate substantially outside the region they were fitted to.

```
Hf_gas = -241.826  # kJ/mol
S_gas = 0.188835   # kJ/mol/K

shomateG = [30.09200,
              6.832514,
              6.793435,
             -2.534480,
              0.082139,
           -250.8810,
            223.3967,
           -241.8264]
```

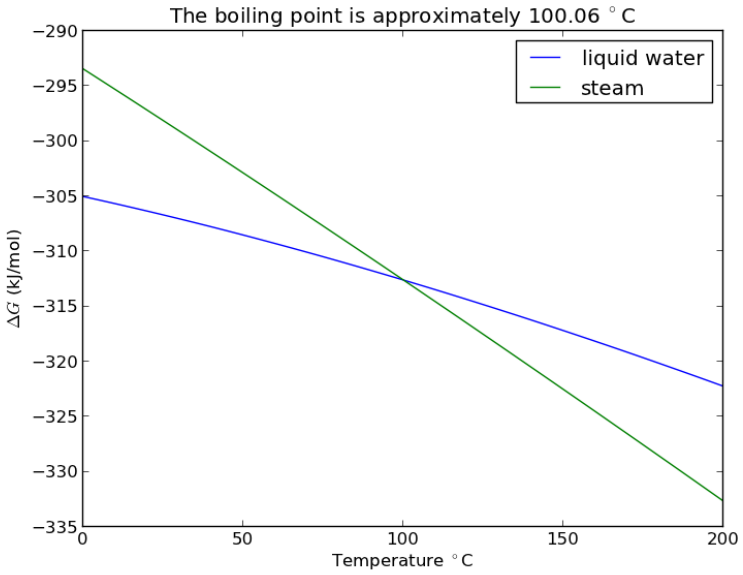
Now, we wan to compute G for each phase as a function of T

```
import numpy as np

T = np.linspace(0, 200) + 273.15
t = T / 1000.0

sTT = np.vstack([np.log(t),
                 t,
                 (t**2) / 2.0,
                 (t**3) / 3.0,
                 -1.0 / (2*t**2),
                 0 * t,
                 t**0,
                 0 * t**0]).T / 1000.0

hTT = np.vstack([t,
                 (t**2)/2.0,
                 (t**3)/3.0,
                 (t**4)/4.0,
                 -1.0 / t,
                 1 * t**0,
                 0 * t**0,
                 -1 * t**0]).T

Gliq = Hf_liq + np.dot(hTT, shomateL) - T*(np.dot(sTT, shomateL))
Ggas = Hf_gas + np.dot(hTT, shomateG) - T*(np.dot(sTT, shomateG))

from scipy.interpolate import interp1d
from scipy.optimize import fsolve

f = interp1d(T, Gliq - Ggas)
bp, = fsolve(f, 373)
print 'The boiling point is {0} K'.format(bp)
```

```
>>> >>> >>> >>> ... ... ... ... ... ... ... >>> >>> ... ... ... ... ... ... ... >>> >>> >>>
```

```
plt.figure(); plt.clf()
plt.plot(T-273.15, Gliq, T-273.15, Ggas)
plt.legend(['liquid water', 'steam'])

plt.xlabel('Temperature $^\circ$C')
plt.ylabel('$\Delta G$ (kJ/mol)')
plt.title('The boiling point is approximately {0:1.2f} $^\circ$C'.format(bp-273.15))
plt.savefig('images/boiling-water.png')
```

```
<matplotlib.figure.Figure object at 0x050D2E30>
[<matplotlib.lines.Line2D object at 0x051AB610>, <matplotlib.lines.Line2D object at 0x051B4
<matplotlib.legend.Legend object at 0x051B9030>
>>> <matplotlib.text.Text object at 0x0519E390>
<matplotlib.text.Text object at 0x050FB390>
<matplotlib.text.Text object at 0x050FBFB0>
```



13.3.1 Summary

The answer we get us 0.05 K too high, which is not bad considering we estimated it using parameters that were fitted to thermodynamic data and that had finite precision and extrapolated the steam properties below the region the parameters were stated to be valid for.

13.4 http://matlab.cheme.cmu.edu/2011/12/25/gibbs-energy-minimization-and-the-nist-webbook/

13.5 http://matlab.cheme.cmu.edu/2011/12/25/finding-equilibrium-composition-by-direct-minimization-of-gibbs-free-energy-on-mole-numbers/

13.6 The Gibbs free energy of a reacting mixture and the equilibrium composition

Matlab post

In this post we derive the equations needed to find the equilibrium composition of a reacting mixture. We use the method of direct minimization of the Gibbs free energy of the reacting mixture.

The Gibbs free energy of a mixture is defined as $G = \sum_j \mu_j n_j$ where μ_j is the chemical potential of species j, and it is temperature and pressure dependent, and n_j is the number of moles of species j.

We define the chemical potential as $\mu_j = G_j^\circ + RT \ln a_j$, where G_j° is the Gibbs energy in a standard state, and a_j is the activity of species j if the pressure and temperature are not at standard state conditions.

If a reaction is occurring, then the number of moles of each species are related to each other through the reaction extent ϵ and stoichiometric coefficients: $n_j = n_{j0} + \nu_j \epsilon$. Note that the reaction extent has units of moles.

Combining these three equations and expanding the terms leads to:

$$G = \sum_j n_{j0} G_j^\circ + \sum_j \nu_j G_j^\circ \epsilon + RT \sum_j (n_{j0} + \nu_j \epsilon) \ln a_j$$

The first term is simply the initial Gibbs free energy that is present before any reaction begins, and it is a constant. It is difficult to evaluate, so we will move it to the left side of the equation in the next step, because it does not matter what its value is since it is a constant. The second term is related to the Gibbs free energy of reaction: $\Delta_r G = \sum_j \nu_j G_j^\circ$. With these observations we rewrite the equation as:

$$G - \sum_j n_{j0} G_j^\circ = \Delta_r G \epsilon + RT \sum_j (n_{j0} + \nu_j \epsilon) \ln a_j$$

Now, we have an equation that allows us to compute the change in Gibbs free energy as a function of the reaction extent, initial number of moles of each species, and the activities of each species. This difference in Gibbs free energy has no natural scale, and depends on the size of the system, i.e. on n_{j0}. It is desirable to avoid this, so we now rescale the equation by the total initial moles present, n_{T0} and define a new variable $\epsilon' = \epsilon / n_{T0}$, which is dimensionless. This leads to:

$$\frac{G - \sum_j n_{j0} G_j^\circ}{n_{T0}} = \Delta_r G \epsilon' + RT \sum_j (y_{j0} + \nu_j \epsilon') \ln a_j$$

where y_{j0} is the initial mole fraction of species j present. The mole fractions are intensive properties that do not depend on the system size. Finally, we need to address a_j. For an ideal gas, we know that $A_j = \frac{y_j P}{P^\circ}$, where the numerator is the partial pressure of species j computed from the mole fraction of species j times the total pressure. To get the mole fraction we note:

$$y_j = \frac{n_j}{n_T} = \frac{n_{j0} + \nu_j \epsilon}{n_{T0} + \epsilon \sum_j \nu_j} = \frac{y_{j0} + \nu_j \epsilon'}{1 + \epsilon' \sum_j \nu_j}$$

This finally leads us to an equation that we can evaluate as a function of reaction extent:

$$\frac{G - \sum_j n_{j0} G_j^\circ}{n_{T0}} = \widetilde{\widetilde{G}} = \Delta_r G \epsilon' + RT \sum_j (y_{j0} + \nu_j \epsilon') \ln \left(\frac{y_{j0} + \nu_j \epsilon'}{1 + \epsilon' \sum_j \nu_j} \frac{P}{P^\circ} \right)$$

we use a double tilde notation to distinguish this quantity from the quantity derived by Rawlings and Ekerdt which is further normalized by a factor of RT. This additional scaling makes the quantities dimensionless, and makes the quantity have a magnitude of order unity, but otherwise has no effect on the shape of the graph.

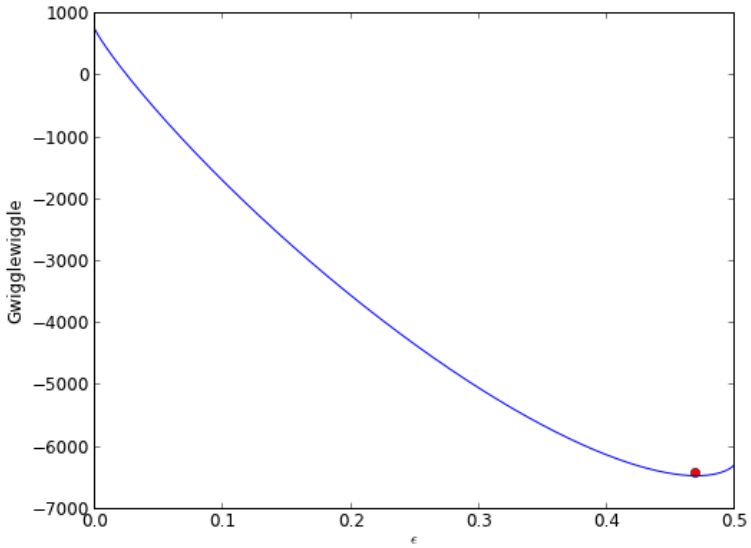
Finally, if we know the initial mole fractions, the initial total pressure, the Gibbs energy of reaction, and the stoichiometric coefficients, we can plot the scaled reacting mixture energy as a function of reaction extent. At equilibrium, this energy will be a minimum. We consider the example in Rawlings and Ekerdt where isobutane (I) reacts with 1-butene (B) to form 2,2,3-trimethylpentane (P). The reaction occurs at a total pressure of 2.5 atm at 400K, with equal molar amounts of I and B. The standard Gibbs free energy of reaction at 400K is -3.72 kcal/mol. Compute the equilibrium composition.

```
import numpy as np

R = 8.314
P = 250000  # Pa
P0 = 100000 # Pa, approximately 1 atm
T = 400 # K

Grxn = -15564.0 #J/mol
yi0 = 0.5; yb0 = 0.5; yp0 = 0.0; # initial mole fractions

yj0 = np.array([yi0, yb0, yp0])
nu_j = np.array([-1.0, -1.0, 1.0])   # stoichiometric coefficients

def Gwigglewiggle(extentp):
    diffg = Grxn * extentp
    sum_nu_j = np.sum(nu_j)
    for i,y in enumerate(yj0):
        x1 = yj0[i] + nu_j[i] * extentp
        x2 = x1 / (1.0 + extentp*sum_nu_j)
        diffg += R * T * x1 * np.log(x2 * P / P0)
    return diffg
```

There are bounds on how large ϵ' can be. Recall that $n_j = n_{j0} + \nu_j \epsilon$, and that $n_j \geq 0$. Thus, $\epsilon_{max} = -n_{j0}/\nu_j$, and the maximum value that ϵ' can have is therefore $-y_{j0}/\nu_j$ where $y_{j0} > 0$. When there are multiple species, you need the smallest $epsilon'_{max}$ to avoid getting negative mole numbers.

```
epsilonp_max = min(-yj0[yj0 > 0] / nu_j[yj0 > 0])
epsilonp = np.linspace(1e-6, epsilonp_max, 1000);

import matplotlib.pyplot as plt

plt.plot(epsilonp,Gwigglewiggle(epsilonp))
plt.xlabel('$\epsilon$')
plt.ylabel('Gwigglewiggle')
plt.savefig('images/gibbs-minim-1.png')
```

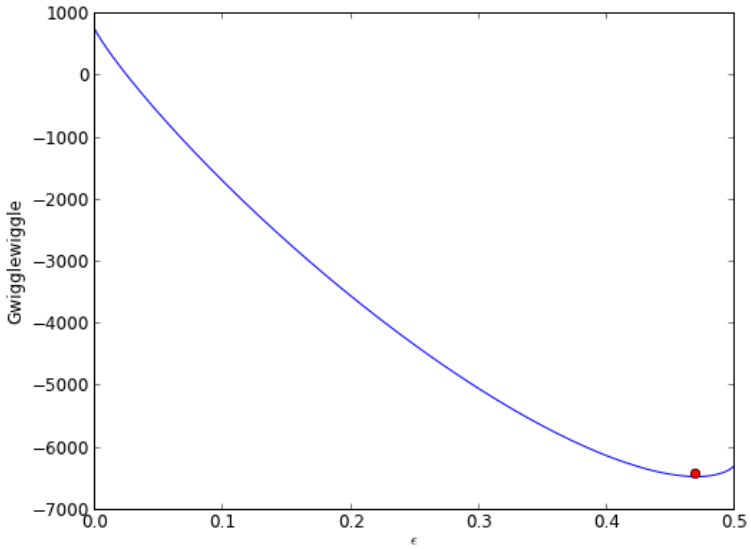
```
>>> [<matplotlib.lines.Line2D object at 0x10a8bf50>]
<matplotlib.text.Text object at 0x10608190>
<matplotlib.text.Text object at 0x10609d10>
```



Now we simply minimize our Gwigglewiggle function. Based on the figure above, the miminum is near 0.45.

```
1  from scipy.optimize import fminbound
2
3  epsilonp_eq = fminbound(Gwigglewiggle, 0, 0.45)
4
5  plt.plot([extmin], [Gwigglewiggle(epsilonp_eq)], 'ro')
6  plt.savefig('images/gibbs-minim-2.png')
```

```
>>> >>> [<matplotlib.lines.Line2D object at 0x10a8b5d0>]
```



To compute equilibrium mole fractions we do this:

```
yi = (yi0 + nu_j[0]*epsilonp_eq) / (1.0 + epsilonp_eq*np.sum(nu_j))
yb = (yb0 + nu_j[1]*epsilonp_eq) / (1.0 + epsilonp_eq*np.sum(nu_j))
yp = (yp0 + nu_j[2]*epsilonp_eq) / (1.0 + epsilonp_eq*np.sum(nu_j))

print yi, yb, yp

# or this
y_j = (yj0 + np.dot(nu_j, epsilonp_eq)) / (1.0 + epsilonp_eq*np.sum(nu_j))
print y_j
```

```
>>> >>> >>> 0.0573226598476 0.0573226598476 0.885354680305
>>> >>> >>> [ 0.05732266  0.05732266  0.88535468]
```

$K = \frac{a_P}{a_I a_B} = \frac{y_p P/P^\circ}{y_i P/P^\circ y_b P/P^\circ} = \frac{y_P}{y_i y_b}\frac{P^\circ}{P}$.

We can express the equilibrium constant like this :$K = \prod_j a_j^{\nu_j}$, and compute it with a single line of code.

```
K = np.exp(-Grxn/R/T)
print K
print yp / (yi * yb) * P0 / P

print np.prod((y_j * P / P0)**nu_j)
```

```
107.776294742
107.776632714
>>> 107.776632714
```

These results are very close, and only disagree because of the default tolerance used in identifying the minimum of our function. you could tighten the tolerances by setting options to the fminbnd function.

13.6.1 Summary

In this post we derived an equation for the Gibbs free energy of a reacting mixture and used it to find the equilibrium composition. In future posts we will examine some alternate forms of the equations that may be more useful in some circumstances.

13.7 Conservation of mass in chemical reactions

Matlab post

Atoms cannot be destroyed in non-nuclear chemical reactions, hence it follows that the same number of atoms entering a reactor must also leave the reactor. The atoms may leave the reactor in a different molecular configuration due to the reaction, but the total mass leaving the reactor must be the same. Here we look at a few ways to show this.

We consider the water gas shift reaction : $CO + H_2O \rightleftharpoons H_2 + CO_2$. We can illustrate the conservation of mass with the following equation: $\nu\mathbf{M} = \mathbf{0}$. Where ν is the stoichiometric coefficient vector and $\mathbf{M}$ is a column vector of molecular weights. For simplicity, we use pure isotope molecular weights, and not the isotope-weighted molecular weights. This equation simply examines the mass on the right side of the equation and the mass on left side of the equation.

```
import numpy as np
nu = [-1, -1, 1, 1];
M = [28, 18, 2, 44];
print np.dot(nu, M)
```

```
0
```

You can see that sum of the stoichiometric coefficients times molecular weights is zero. In other words a CO and H_2O have the same mass as H_2 and CO_2.

For any balanced chemical equation, there are the same number of each kind of atom on each side of the equation. Since the mass of each atom is unchanged with reaction, that means the mass of all the species that are reactants must equal the mass of all the species that are products! Here we look at the number of C, O, and H on each side of the reaction. Now if we add the mass of atoms in the reactants and products, it should sum to zero (since we used the negative sign for stoichiometric coefficients of reactants).

```
import numpy as np
            # C   O   H
reactants = [-1, -2, -2]
products  = [ 1,  2,  2]
```

```
5
6   atomic_masses = [12.011, 15.999, 1.0079]  # atomic masses
7
8   print np.dot(reactants, atomic_masses) + np.dot(products, atomic_masses)
```

```
>>> ... >>> >>> >>> >>> >>> 0.0
```

That is all there is to mass conservation with reactions. Nothing changes if there are lots of reactions, as long as each reaction is properly balanced, and none of them are nuclear reactions!

13.8 Water gas shift equilibria via the NIST Webbook

Matlab post

The NIST webbook provides parameterized models of the enthalpy, entropy and heat capacity of many molecules. In this example, we will examine how to use these to compute the equilibrium constant for the water gas shift reaction $CO + H_2O \rightleftharpoons CO_2 + H_2$ in the temperature range of 500K to 1000K.

Parameters are provided for:

Cp = heat capacity (J/mol*K) H = standard enthalpy (kJ/mol) S = standard entropy (J/mol*K)

with models in the form: $Cp^\circ = A + B*t + C*t^2 + D*t^3 + E/t^2$

$H^\circ - H^\circ_{298.15} = A*t + B*t^2/2 + C*t^3/3 + D*t^4/4 - E/t + F - H$

$S^\circ = A*ln(t) + B*t + C*t^2/2 + D*t^3/3 - E/(2*t^2) + G$

where $t = T/1000$, and T is the temperature in Kelvin. We can use this data to calculate equilibrium constants in the following manner. First, we have heats of formation at standard state for each compound; for elements, these are zero by definition, and for non-elements, they have values available from the NIST webbook. There are also values for the absolute entropy at standard state. Then, we have an expression for the change in enthalpy from standard state as defined above, as well as the absolute entropy. From these we can derive the reaction enthalpy, free energy and entropy at standard state, as well as at other temperatures.

We will examine the water gas shift enthalpy, free energy and equilibrium constant from 500K to 1000K, and finally compute the equilibrium composition of a gas feed containing 5 atm of CO and H_2 at 1000K.

```
1   import numpy as np
2
3   T = np.linspace(500,1000) # degrees K
4   t = T/1000;
```

13.8.1 hydrogen

[[http://webbook.nist.gov/cgi/cbook.cgi?ID=C1333740&Units=SI&Mask=1#Thermo-Gas][http://webbook.nist.gov/cgi/cbook.cgi?ID=C1333740&Units=SI&Mask=1#Thermo-Gas]]

```
# T = 298-1000K valid temperature range
A =  33.066178
B = -11.363417
C =  11.432816
D = -2.772874
E = -0.158558
F = -9.980797
G =  172.707974
H =  0.0

Hf_29815_H2 = 0.0 # kJ/mol
S_29815_H2 = 130.68 # J/mol/K

dH_H2 = A*t + B*t**2/2 + C*t**3/3 + D*t**4/4 - E/t + F - H;
S_H2 = (A*np.log(t) + B*t + C*t**2/2 + D*t**3/3 - E/(2*t**2) + G);
```

13.8.2 H_2O

[[http://webbook.nist.gov/cgi/cbook.cgi?ID=C7732185&Units=SI&Mask=1#Thermo-Gas][http://webbook.nist.gov/cgi/cbook.cgi?ID=C7732185&Units=SI&Mask=1#Thermo-Gas]]

Note these parameters limit the temperature range we can examine, as these parameters are not valid below 500K. There is another set of parameters for lower temperatures, but we do not consider them here.

```
# 500-1700 K valid temperature range
A =   30.09200
B =   6.832514
C =   6.793435
D =  -2.534480
E =   0.082139
F =  -250.8810
G =   223.3967
H =  -241.8264

Hf_29815_H2O = -241.83 #this is Hf.
S_29815_H2O = 188.84

dH_H2O = A*t + B*t**2/2 + C*t**3/3 + D*t**4/4 - E/t + F - H;
S_H2O = (A*np.log(t) + B*t + C*t**2/2 + D*t**3/3 - E/(2*t**2) + G);
```

13.8.3 CO

[[http://webbook.nist.gov/cgi/cbook.cgi?ID=C630080&Units=SI&Mask=1#Thermo-Gas][http://webbook.nist.gov/cgi/cbook.cgi?ID=C630080&Units=SI&Mask=1#Thermo-Gas]]

```
# 298. - 1300K valid temperature range
A =   25.56759
B =   6.096130
C =   4.054656
D =  -2.671301
E =   0.131021
F =  -118.0089
G =   227.3665
H = -110.5271

```

```
Hf_29815_CO = -110.53 #this is Hf kJ/mol.
S_29815_CO = 197.66

dH_CO = A*t + B*t**2/2 + C*t**3/3 + D*t**4/4 - E/t + F - H;
S_CO = (A*np.log(t) + B*t + C*t**2/2 + D*t**3/3 - E/(2*t**2) + G);
```

13.8.4 CO_2

[[http://webbook.nist.gov/cgi/cbook.cgi?ID=C124389&Units=SI&Mask=1#Thermo-Gas][http://webbook.nist.gov/cgi/cbook.cgi?ID=C124389&Units=SI&Mask=1#Thermo-Gas]]

```
# 298. - 1200.K valid temperature range
A =   24.99735
B =   55.18696
C =  -33.69137
D =   7.948387
E =  -0.136638
F =  -403.6075
G =   228.2431
H =  -393.5224

Hf_29815_CO2 = -393.51 # this is Hf.
S_29815_CO2 = 213.79

dH_CO2 = A*t + B*t**2/2 + C*t**3/3 + D*t**4/4 - E/t + F - H;
S_CO2 = (A*np.log(t) + B*t + C*t**2/2 + D*t**3/3 - E/(2*t**2) + G);
```

13.8.5 Standard state heat of reaction

We compute the enthalpy and free energy of reaction at 298.15 K for the following reaction $CO + H2O \rightleftharpoons H2 + CO2$.

```
Hrxn_29815 = Hf_29815_CO2 + Hf_29815_H2 - Hf_29815_CO - Hf_29815_H2O;
Srxn_29815 = S_29815_CO2 + S_29815_H2 - S_29815_CO - S_29815_H2O;
Grxn_29815 = Hrxn_29815 - 298.15*(Srxn_29815)/1000;

print('deltaH = {0:1.2f}'.format(Hrxn_29815))
print('deltaG = {0:1.2f}'.format(Grxn_29815))
```

```
>>> >>> >>> deltaH = -41.15
deltaG = -28.62
```

13.8.6 Non-standard state ΔH and ΔG

We have to correct for temperature change away from standard state. We only correct the enthalpy for this temperature change. The correction looks like this:

$$\Delta H_{rxn}(T) = \Delta H_{rxn}(T_{ref}) + \sum_i \nu_i (H_i(T) - H_i(T_{ref}))$$

Where ν_i are the stoichiometric coefficients of each species, with appropriate sign for reactants and products, and $(H_i(T) - H_i(T_{ref})$ is precisely what is calculated for each species with the equations

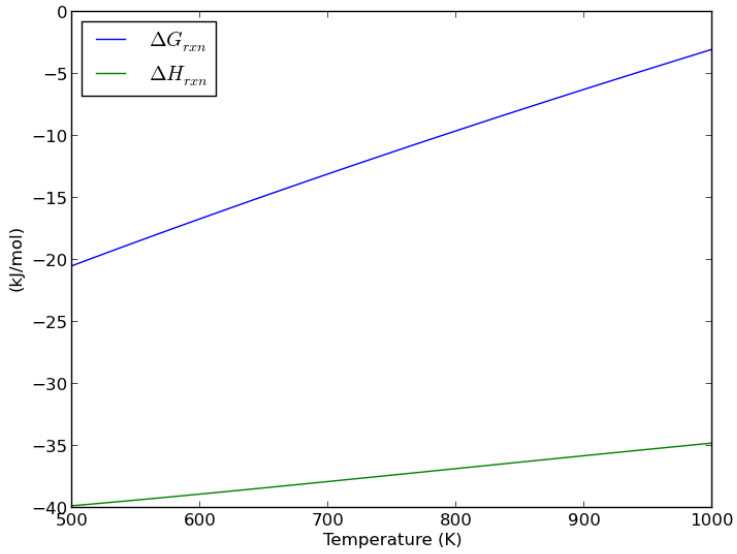
The entropy is on an absolute scale, so we directly calculate entropy at each temperature. Recall that H is in kJ/mol and S is in J/mol/K, so we divide S by 1000 to make the units match.

```
Hrxn = Hrxn_29815 + dH_CO2 + dH_H2 - dH_CO - dH_H2O
Grxn = Hrxn - T*(S_CO2 + S_H2 - S_CO - S_H2O)/1000
```

13.8.7 Plot how the ΔG varies with temperature

```
import matplotlib.pyplot as plt
plt.figure(); plt.clf()
plt.plot(T,Grxn, label='$\Delta G_{rxn}$')
plt.plot(T,Hrxn, label='$\Delta H_{rxn}$')
plt.xlabel('Temperature (K)')
plt.ylabel('(kJ/mol)')
plt.legend( loc='best')
plt.savefig('images/wgs-nist-1.png')
```

```
<matplotlib.figure.Figure object at 0x04199CF0>
[<matplotlib.lines.Line2D object at 0x0429BF30>]
[<matplotlib.lines.Line2D object at 0x0427DFB0>]
<matplotlib.text.Text object at 0x041B79F0>
<matplotlib.text.Text object at 0x040CEF70>
<matplotlib.legend.Legend object at 0x043CB5F0>
```



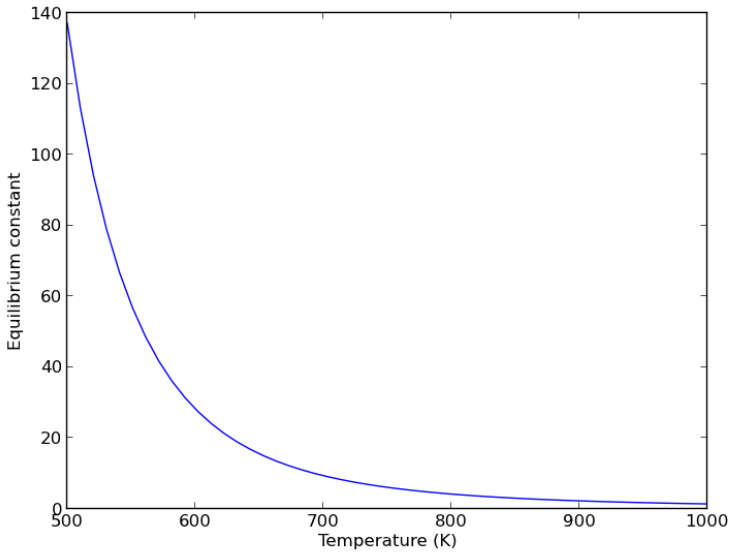
Over this temperature range the reaction is exothermic, although near 1000K it is just barely exothermic. At higher temperatures we expect the reaction to become endothermic.

13.8.8 Equilibrium constant calculation

Note the equilibrium constant starts out high, i.e. strongly favoring the formation of products, but drops very quicky with increasing temperature.

```
R = 8.314e-3 # kJ/mol/K
K = np.exp(-Grxn/R/T);

plt.figure()
plt.plot(T,K)
plt.xlim([500, 1000])
plt.xlabel('Temperature (K)')
plt.ylabel('Equilibrium constant')
plt.savefig('images/wgs-nist-2.png')
```

```
>>> >>> <matplotlib.figure.Figure object at 0x044DBE90>
[<matplotlib.lines.Line2D object at 0x045A53F0>]
(500, 1000)
<matplotlib.text.Text object at 0x04577470>
<matplotlib.text.Text object at 0x0457F410>
```



13.8.9 Equilibrium yield of WGS

Now let us suppose we have a reactor with a feed of H_2O and CO at 10atm at 1000K. What is the equilibrium yield of H_2? Let ϵ be the extent of reaction, so that $F_i = F_{i,0} + \nu_i \epsilon$. For reactants, ν_i is negative, and for products, ν_i is positive. We have to solve for the extent of reaction that satisfies the equilibrium condition.

```
from scipy.interpolate import interp1d
from scipy.optimize import fsolve

#
# A = CO
# B = H2O
# C = H2
# D = CO2

Pa0 = 5; Pb0 = 5; Pc0 = 0; Pd0 = 0;  # pressure in atm
R = 0.082;
Temperature = 1000;

# we can estimate the equilibrium like this. We could also calculate it
# using the equations above, but we would have to evaluate each term. Above
# we simply computed a vector of enthalpies, entropies, etc... Here we interpolate
K_func = interp1d(T,K);
K_Temperature = K_func(1000)


# If we let X be fractional conversion then we have £C_A = C_{A0}(1-X)£,
# £C_B = C_{B0}-C_{A0}X£, £C_C = C_{C0}+C_{A0}X£, and £C_D =
# C_{D0}+C_{A0}X£. We also have £K(T) = (C_C C_D)/(C_A C_B)£, which finally
# reduces to £0 = K(T) - Xeq^2/(1-Xeq)^2£ under these conditions.

def f(X):
    return K_Temperature - X**2/(1-X)**2;

x0 = 0.5
Xeq, = fsolve(f, x0)

print('The equilibrium conversion for these feed conditions is: {0:1.2f}'.format(Xeq))
```

```
>>> >>> ... ... ... ... ... >>> >>> >>> >>> >>> ... ... ... >>> >>> >>> >>> ... ... ... ...
The equilibrium conversion for these feed conditions is: 0.55
```

13.8.10 Compute gas phase pressures of each species

Since there is no change in moles for this reaction, we can directly calculation the pressures from the equilibrium conversion and the initial pressure of gases. you can see there is a slightly higher pressure of H_2 and CO_2 than the reactants, consistent with the equilibrium constant of about 1.44 at 1000K. At a lower temperature there would be a much higher yield of the products. For example, at 550K the equilibrium constant is about 58, and the pressure of H_2 is 4.4 atm due to a much higher equilibrium conversion of 0.88.

```
P_CO = Pa0*(1-Xeq)
P_H2O = Pa0*(1-Xeq)
P_H2 = Pa0*Xeq
P_CO2 = Pa0*Xeq

print P_CO,P_H2O, P_H2, P_CO2
```

```
>>> >>> >>> >>> 2.2747854428 2.2747854428 2.7252145572 2.7252145572
```

13.8.11 Compare the equilibrium constants

We can compare the equilibrium constant from the Gibbs free energy and the one from the ratio of pressures. They should be the same!

```
print K_Temperature
print (P_CO2*P_H2)/(P_CO*P_H2O)
```

```
1.43522674762
1.43522674762
```

They are the same.

13.8.12 Summary

The NIST Webbook provides a plethora of data for computing thermodynamic properties. It is a little tedious to enter it all into Matlab, and a little tricky to use the data to estimate temperature dependent reaction energies. A limitation of the Webbook is that it does not tell you have the thermodynamic properties change with pressure. Luckily, those changes tend to be small.

I noticed a different behavior in interpolation between scipy.interpolate.interp1d and Matlab's interp1. The scipy function returns an interpolating function, whereas the Matlab function directly interpolates new values, and returns the actual interpolated data.

13.9 Numerically calculating an effectiveness factor for a porous catalyst bead

Matlab post

If reaction rates are fast compared to diffusion in a porous catalyst pellet, then the observed kinetics will appear to be slower than they really are because not all of the catalyst surface area will be effectively used. For example, the reactants may all be consumed in the near surface area of a catalyst bead, and the inside of the bead will be unutilized because no reactants can get in due to the high reaction rates.

References: Ch 12. Elements of Chemical Reaction Engineering, Fogler, 4th edition.

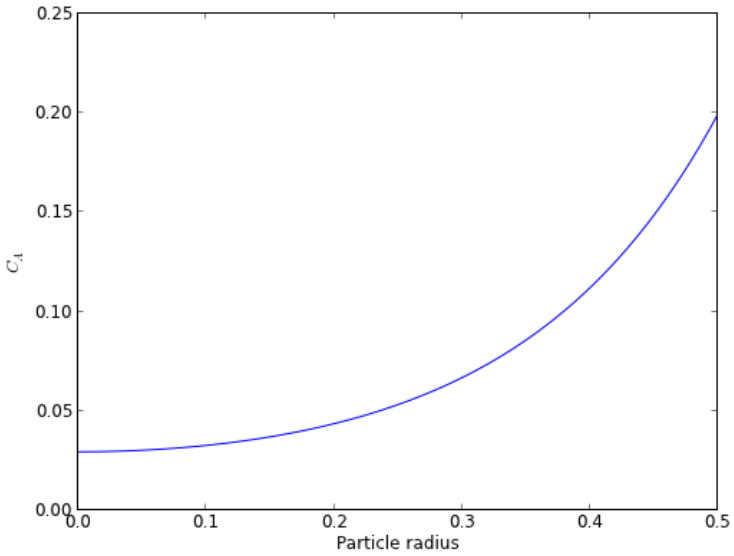
A mole balance on the particle volume in spherical coordinates with a first order reaction leads to: $\frac{d^2Ca}{dr^2} + \frac{2}{r}\frac{dCa}{dr} - \frac{k}{D_e}C_A = 0$ with boundary conditions $C_A(R) = C_{As}$ and $\frac{dCa}{dr} = 0$ at $r = 0$. We convert this equation to a system of first order ODEs by letting $W_A = \frac{dCa}{dr}$.

We have a condition of no flux at r=0 and Ca(R) = CAs, which makes this a boundary value problem. We use the shooting method here, and guess what Ca(0) is and iterate the guess to get Ca(R) = CAs.

```
import numpy as np
from scipy.integrate import odeint
```

```
import matplotlib.pyplot as plt

De = 0.1    # diffusivity cm^2/s
R  = 0.5    # particle radius, cm
k  = 6.4    # rate constant (1/s)
CAs = 0.2   # concentration of A at outer radius of particle (mol/L)

def ode(Y, r):
    Wa = Y[0] # molar rate of delivery of A to surface of particle
    Ca = Y[1] # concentration of A in the particle at r

    if r == 0:
        dWadr = 0   #this solves the singularity at r = 0
    else:
        dWadr = -2*Wa/r + k/De*Ca

    dCadr = Wa

    return [dWadr, dCadr]

# Initial conditions
Ca0 = 0.029315 # Ca(0) (mol/L) guessed to satisfy Ca(R) = CAs
Wa0 = 0        # no flux at r=0 (mol/m^2/s)

rspan = np.linspace(0, R, 500)

Y = odeint(ode, [Wa0, Ca0], rspan)

Ca = Y[:,1]

# here we check that Ca(R) = Cas
print 'At r={0} Ca={1}'.format(rspan[-1],Ca[-1])

plt.plot(rspan, Ca)
plt.xlabel('Particle radius')
plt.ylabel('$C_A$')
plt.savefig('images/effectiveness-factor.png')

r = rspan
eta_numerical = np.trapz(k*Ca*4*np.pi*(r**2), r)/np.trapz(k*CAs*4*np.pi*(r**2), r)
print eta_numerical

phi = R*np.sqrt(k/De);
eta_analytical = (3/phi**2)*(phi*(1.0 / np.tanh(phi))-1)
print eta_analytical
```

```
At r=0.5 Ca=0.200001488652
0.563011348314
0.563003362801
```



You can see the concentration of A inside the particle is significantly lower than outside the particle. That is because it is reacting away faster than it can diffuse into the particle. Hence, the overall reaction rate in the particle is lower than it would be without the diffusion limit.

The effectiveness factor is the ratio of the actual reaction rate in the particle with diffusion limitation to the ideal rate in the particle if there was no concentration gradient:

$$\eta = \frac{\int_0^R k'' a C_A(r) 4\pi r^2 dr}{\int_0^R k'' a C_{As} 4\pi r^2 dr}$$

We will evaluate this numerically from our solution and compare it to the analytical solution. The results are in good agreement, and you can make the numerical estimate better by increasing the number of points in the solution so that the numerical integration is more accurate.

Why go through the numerical solution when an analytical solution exists? The analytical solution here is only good for 1st order kinetics in a sphere. What would you do for a complicated rate law? You might be able to find some limiting conditions where the analytical equation above is relevant, and if you are lucky, they are appropriate for your problem. If not, it is a good thing you can figure this out numerically!

13.10 Computing a pipe diameter

Matlab post A heat exchanger must handle 2.5 L/s of water through a smooth pipe with length of 100 m. The pressure drop cannot exceed 103 kPa at 25 degC. Compute the minimum pipe diameter required for this application.

Adapted from problem 8.8 in Problem solving in chemical and Biochemical Engineering with Polymath, Excel, and Matlab. page 303.

We need to estimate the Fanning friction factor for these conditions so we can estimate the frictional losses that result in a pressure drop for a uniform, circular pipe. The frictional forces are given by $F_f = 2 f_F \frac{\Delta L v^2}{D}$, and the corresponding pressure drop is given by $\Delta P = \rho F_f$. In these equations, ρ is the fluid density, v is the fluid velocity, D is the pipe diameter, and f_F is the Fanning friction factor. The average fluid velocity is given by $v = \frac{q}{\pi D^2/4}$.

For laminar flow, we estimate $f_F = 16/Re$, which is a linear equation, and for turbulent flow ($Re > 2100$) we have the implicit equation $\frac{1}{\sqrt{f_F}} = 4.0 \log(Re\sqrt{f_F}) - 0.4$. Of course, we define $Re = \frac{Dv\rho}{\mu}$ where μ is the viscosity of the fluid.

It is known that $\rho(T) = 46.048 + 9.418T - 0.0329T^2 + 4.882 \times 10^{-5} - 2.895 \times 10^{-8}T^4$ and $\mu = \exp\left(-10.547 + \frac{541.69}{T - 144.53}\right)$ where ρ is in kg/mˆ3 and μ is in kg/(m*s).

The aim is to find D that solves: $\Delta p = \rho 2 f_F \frac{\Delta L v^2}{D}$. This is a nonlinear equation in D, since D affects the fluid velocity, the Re, and the Fanning friction factor. Here is the solution

```
import numpy as np
from scipy.optimize import fsolve
import matplotlib.pyplot as plt

T = 25 + 273.15
Q = 2.5e-3       # mˆ3/s
deltaP = 103000  # Pa
deltaL = 100     # m

#Note these correlations expect dimensionless T, where the magnitude
# of T is in K

def rho(T):
    return 46.048 + 9.418 * T -0.0329 * T**2 +4.882e-5 * T**3 - 2.895e-8 * T**4

def mu(T):
    return np.exp(-10.547 + 541.69 / (T - 144.53))

def fanning_friction_factor_(Re):
    if Re < 2100:
        raise Exception('Flow is probably not turbulent, so this correlation is not appropriate.')
    # solve the Nikuradse correlation to get the friction factor
    def fz(f): return 1.0/np.sqrt(f) - (4.0*np.log10(Re*np.sqrt(f))-0.4)
    sol, = fsolve(fz, 0.01)
    return sol

fanning_friction_factor = np.vectorize(fanning_friction_factor_)

Re = np.linspace(2200, 9000)
f = fanning_friction_factor(Re)

plt.plot(Re, f)
plt.xlabel('Re')
plt.ylabel('fanning friction factor')
# You can see why we use 0.01 as an initial guess for solving for the
# Fanning friction factor; it falls in the middle of ranges possible
# for these Re numbers.
plt.savefig('images/pipe-diameter-1.png')
```

```
39
40  def objective(D):
41      v = Q / (np.pi * D**2 / 4)
42      Re = D * v * rho(T) / mu(T)
43
44      fF = fanning_friction_factor(Re)
45
46      return deltaP - 2 * fF * rho(T) * deltaL * v**2 / D
47
48  D, = fsolve(objective, 0.04)
49
50  print('The minimum pipe diameter is {0} m\n'.format(D))
```

```
The minimum pipe diameter is 0.0389653369531 m
```

Any pipe diameter smaller than that value will result in a larger pressure drop at the same volumetric flow rate, or a smaller volumetric flowrate at the same pressure drop. Either way, it will not meet the design specification.

13.11 Reading parameter database text files in python

Matlab post

The datafile at http://terpconnect.umd.edu/ñsw/ench250/antoine.dat (dead link) contains data that can be used to estimate the vapor pressure of about 700 pure compounds using the Antoine equation

The data file has the following contents:

```
Antoine Coefficients
  log(P) = A-B/(T+C) where P is in mmHg and T is in Celsius
Source of data: Yaws and Yang (Yaws, C.  L.  and Yang, H.  C.,
"To estimate vapor pressure easily. antoine coefficients relate vapor pressure to temperatu

ID  formula  compound name                   A       B       C     Tmin Tmax ??    ?
-------------------------------------------------------------------------------------
  1 CCL4     carbon-tetrachloride        6.89410 1219.580 227.170  -20  101 Y2    0
  2 CCL3F    trichlorofluoromethane      6.88430 1043.010 236.860  -33   27 Y2    0
  3 CCL2F2   dichlorodifluoromethane     6.68619  782.072 235.377 -119  -30 Y6    0
```

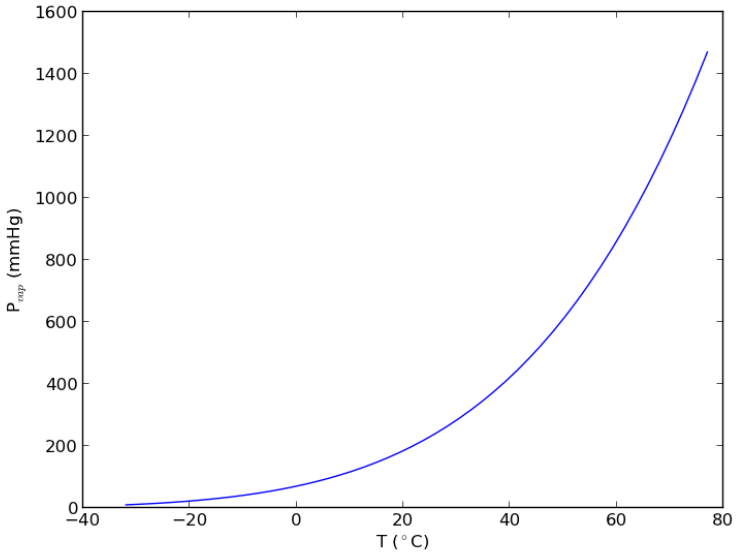
To use this data, you find the line that has the compound you want, and read off the data. You could do that manually for each component you want but that is tedious, and error prone. Today we will see how to retrieve the file, then read the data into python to create a database we can use to store and retrieve the data.

We will use the data to find the temperature at which the vapor pressure of acetone is 400 mmHg.

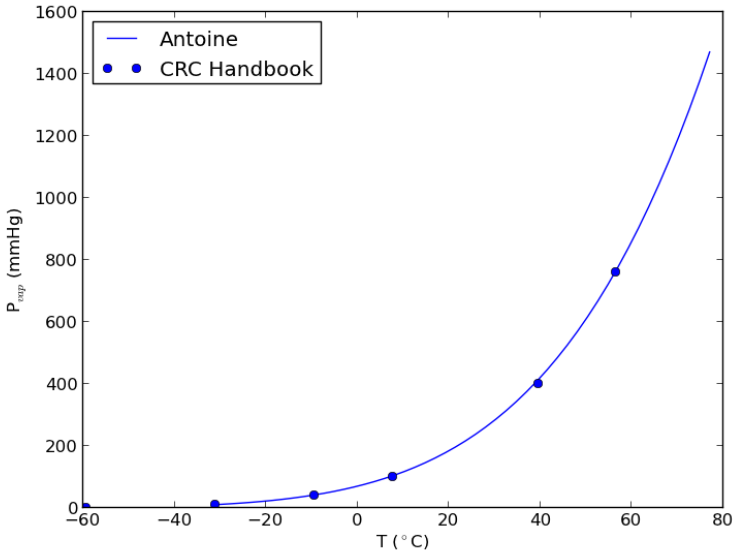
We use numpy.loadtxt to read the file, and tell the function the format of each column. This creates a special kind of record array which we can access data by field name.

```
import numpy as np
import matplotlib.pyplot as plt

data = np.loadtxt('data/antoine_data.dat',
                  dtype=[('id', np.int),
                         ('formula', 'S8'),
                         ('name', 'S28'),
                         ('A', np.float),
                         ('B', np.float),
                         ('C', np.float),
                         ('Tmin', np.float),
                         ('Tmax', np.float),
                         ('??', 'S4'),
                         ('?', 'S4')],
                  skiprows=7)

names = data['name']

acetone, = data[names == 'acetone']

# for readability we unpack the array into variables
id, formula, name, A, B, C, Tmin, Tmax, u1, u2 = acetone

T = np.linspace(Tmin, Tmax)
P = 10**(A - B / ( T + C))
plt.plot(T, P)
plt.xlabel('T ($^\circ$C)')
plt.ylabel('P$_{vap}$ (mmHg)')

# Find T at which Pvap = 400 mmHg
# from our graph we might guess T ~ 40 ^{\circ}C

def objective(T):
    return 400 - 10**(A - B / (T + C))

from scipy.optimize import fsolve
Tsol, = fsolve(objective, 40)
print Tsol
print 'The vapor pressure is 400 mmHg at T = {0:1.1f} degC'.format(Tsol)

#Plot CRC data http://en.wikipedia.org/wiki/Acetone_%28data_page%29#Vapor_pressure_of_liquid
# We only include the data for the range where the Antoine fit is valid.

Tcrc  = [-59.4,         -31.1,  -9.4,   7.7,    39.5,   56.5]
Pcrc = [        1,      10,     40,     100,    400,    760]

plt.plot(Tcrc, Pcrc, 'bo')
plt.legend(['Antoine','CRC Handbook'], loc='best')
plt.savefig('images/antoine-2.png')
```

```
38.6138198197
The vapor pressure is 400 mmHg at T = 38.6 degC
```



This result is close to the value reported here (39.5 degC), from the CRC Handbook. The difference is probably that the value reported in the CRC is an actual experimental number.



13.12 Calculating a bubble point pressure of a mixture

Matlab post

Adapted from http://terpconnect.umd.edu/ñsw/ench250/bubpnt.htm (dead link)

We previously learned to read a datafile containing lots of Antoine coefficients into a database, and use the coefficients to estimate vapor pressure of a single compound. Here we use those coefficents to compute a bubble point pressure of a mixture.

The bubble point is the temperature at which the sum of the component vapor pressures is equal to the the total pressure. This is where a bubble of vapor will first start forming, and the mixture starts to boil.

Consider an equimolar mixture of benzene, toluene, chloroform, acetone and methanol. Compute the bubble point at 760 mmHg, and the gas phase composition. The gas phase composition is given by: $y_i = x_i * P_i / P_T$.

```
import numpy as np
from scipy.optimize import fsolve

# load our thermodynamic data
data = np.loadtxt('data/antoine_data.dat',
                  dtype=[('id', np.int),
                         ('formula', 'S8'),
                         ('name', 'S28'),
                         ('A', np.float),
                         ('B', np.float),
                         ('C', np.float),
                         ('Tmin', np.float),
                         ('Tmax', np.float),
                         ('??', 'S4'),
                         ('?', 'S4')],
                  skiprows=7)

compounds = ['benzene', 'toluene', 'chloroform', 'acetone', 'methanol']

# extract the data we want
A = np.array([data[data['name'] == x]['A'][0] for x in compounds])
B = np.array([data[data['name'] == x]['B'][0] for x in compounds])
C = np.array([data[data['name'] == x]['C'][0] for x in compounds])
Tmin = np.array([data[data['name'] == x]['Tmin'][0] for x in compounds])
Tmax = np.array([data[data['name'] == x]['Tmax'][0] for x in compounds])


# we have an equimolar mixture
x = np.array([0.2, 0.2, 0.2, 0.2, 0.2])

# Given a T, we can compute the pressure of each species like this:

T = 67 # degC
P = 10**(A - B / (T + C))
print P
print np.dot(x, P)  # total mole-fraction weighted pressure

Tguess = 67
Ptotal = 760

def func(T):
    P = 10**(A - B / (T + C))
    return Ptotal - np.dot(x, P)

Tbubble, = fsolve(func, Tguess)
```

```
46
47  print 'The bubble point is {0:1.2f} degC'.format(Tbubble)
48
49  # double check answer is in a valid T range
50  if np.any(Tbubble < Tmin) or np.any(Tbubble > Tmax):
51      print 'T_bubble is out of range!'
52
53  # print gas phase composition
54  y = x * 10**(A - B / (Tbubble + C))/Ptotal
55
56  for cmpd, yi in zip(compounds, y):
57      print 'y_{0:<10s} = {1:1.3f}'.format(cmpd, yi)
```

```
[  498.4320267    182.16010994   898.31061294  1081.48181768   837.88860027]
699.654633507
The bubble point is 69.46 degC
y_benzene    = 0.142
y_toluene    = 0.053
y_chloroform = 0.255
y_acetone    = 0.308
y_methanol   = 0.242
```

13.13 The equal area method for the van der Waals equation

Matlab post

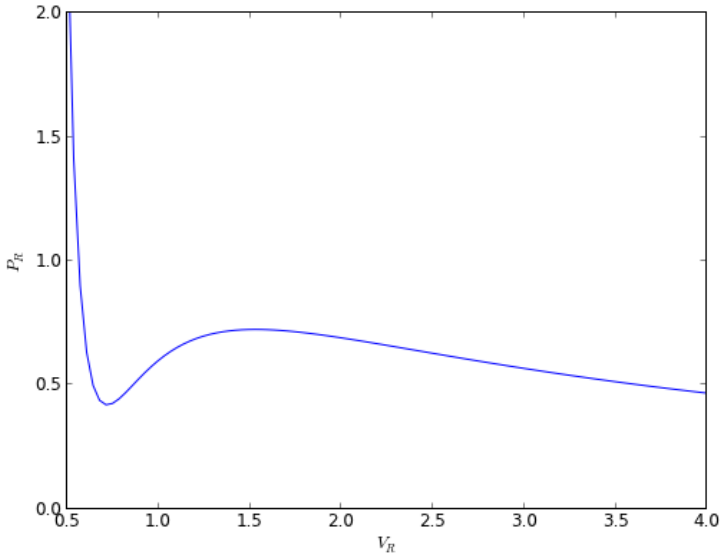
When a gas is below its Tc the van der Waal equation oscillates. In the portion of the isotherm where $\partial P_R/\partial V_r > 0$, the isotherm fails to describe real materials, which phase separate into a liquid and gas in this region.

Maxwell proposed to replace this region by a flat line, where the area above and below the curves are equal. Today, we examine how to identify where that line should be.

```
1   import numpy as np
2   import matplotlib.pyplot as plt
3
4   Tr = 0.9 # A Tr below Tc:  Tr = T/Tc
5   # analytical equation for Pr. This is the reduced form of the van der Waal
6   # equation.
7   def Prfh(Vr):
8       return  8.0 / 3.0 * Tr / (Vr - 1.0 / 3.0) - 3.0 / (Vr**2)
9
10  Vr = np.linspace(0.5, 4, 100)  # vector of reduced volume
11  Pr = Prfh(Vr)                  # vector of reduced pressure
12
13  plt.plot(Vr,Pr)
14  plt.ylim([0, 2])
15  plt.xlabel('$V_R$')
16  plt.ylabel('$P_R$')
17  plt.savefig('images/maxwell-eq-area-1.png')
```

```
>>> >>> >>> ... ... ... ... >>> >>> >>> >>> [<matplotlib.lines.Line2D object at 0x1f74b2d0>
(0, 2)
```

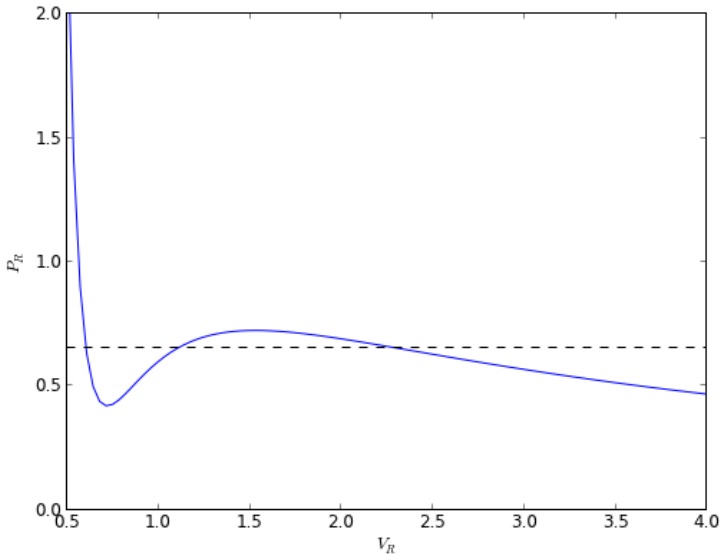
```
<matplotlib.text.Text object at 0x1f3d97d0>
<matplotlib.text.Text object at 0x1f3de210>
```



The idea is to pick a Pr and draw a line through the EOS. We want the areas between the line and EOS to be equal on each side of the middle intersection.

```
y = 0.65

plt.plot([0.5, 4.0], [y, y], 'k--')
plt.savefig('images/maxwell-eq-area-2.png')
```

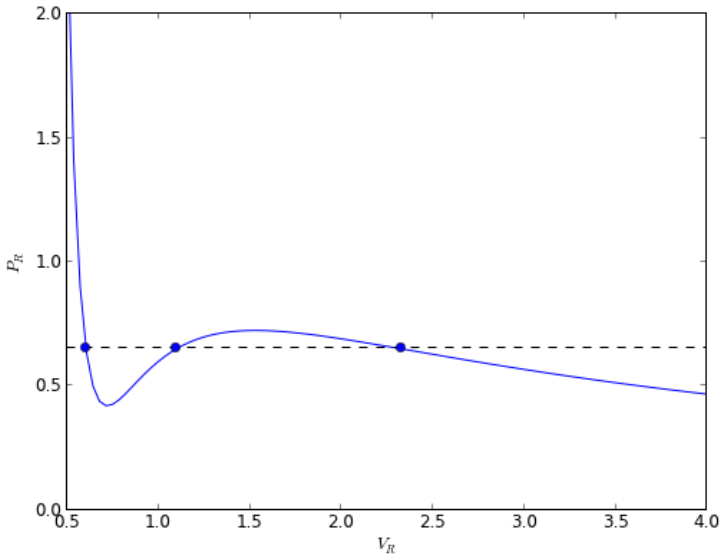
```
>>> [<matplotlib.lines.Line2D object at 0x1f74bb90>]
```



To find the areas, we need to know where the intersection of the vdW eqn with the horizontal line. This is the same as asking what are the roots of the vdW equation at that Pr. We need all three intersections so we can integrate from the first root to the middle root, and then the middle root to the third root. We take advantage of the polynomial nature of the vdW equation, which allows us to use the roots command to get all the roots at once. The polynomial is $V_R^3 - \frac{1}{3}(1 + 8T_R/P_R) + 3/P_R - 1/P_R = 0$. We use the coefficients t0 get the roots like this.

```
vdWp = [1.0, -1. / 3.0 * (1.0 + 8.0 * Tr / y), 3.0 / y, - 1.0 / y];
v = np.roots(vdWp)
v.sort()
print v

plt.plot(v[0], y, 'bo', v[1], y, 'bo', v[2], y, 'bo')
plt.savefig('images/maxwell-eq-area-3.png')
```

```
>>> >>> [ 0.60286812  1.09743234  2.32534056]
>>> [<matplotlib.lines.Line2D object at 0x1f87efd0>, <matplotlib.lines.Line2D object at 0x1
```



13.13.1 Compute areas

for A1, we need the area under the line minus the area under the vdW curve. That is the area between the curves. For A2, we want the area under the vdW curve minus the area under the line. The area under the line between root 2 and root 1 is just the width (root2 - root1)*y

```
from scipy.integrate import quad

A1, e1 = (v[1] - v[0]) * y - quad(Prfh,  v[0], v[1])
A2, e2 = quad(Prfh, v[1], v[2]) - (v[2] - v[1]) * y

print A1, A2
print e1, e2  # interesting these look so large
```

```
>>> 0.063225945606 0.0580212098122
0.321466743765 -0.798140339268
```

```
from scipy.optimize import fsolve

def equal_area(y):
    Tr = 0.9
    vdWp = [1, -1.0 / 3 * ( 1.0 + 8.0 * Tr / y), 3.0 / y,  -1.0 / y]
    v = np.roots(vdWp)
    v.sort()
    A1 = (v[1] - v[0]) * y - quad(Prfh, v[0], v[1])
    A2 = quad(Prfh, v[1], v[2]) - (v[2] - v[1]) * y
    return  A1 - A2

y_eq, = fsolve(equal_area, 0.65)
```

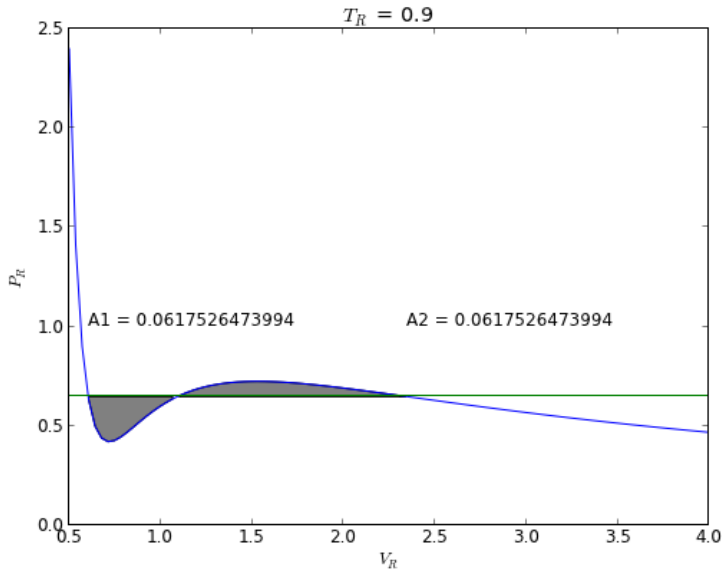
```
print y_eq

A1, e1 = (v[1] - v[0]) * y_eq - quad(Prfh,  v[0], v[1])
A2, e2 = quad(Prfh, v[1], v[2]) - (v[2] - v[1]) * y_eq

vdWp = [1.0, -1.0 / 3.0 * (1.0 + 8.0 * Tr / y_eq), 3.0 / y_eq, -1.0 / y_eq]
v = np.roots(vdWp)
v.sort()

print v
```

```
... ... ... ... 0.646998351872
>>> >>> >>> >>> >>> [ 0.6034019   1.09052663  2.34884238]
```

Now let us plot the equal areas and indicate them by shading.

```
fig = plt.figure()
plt.clf()
ax = fig.add_subplot(111)

ax.plot(Vr,Pr)

hline = np.ones(Vr.size) * y_eq

ax.plot(Vr, hline)
ax.fill_between(Vr, hline, Pr, where=(Vr >= v[0]) & (Vr <= v[1]), facecolor='gray')
ax.fill_between(Vr, hline, Pr, where=(Vr >= v[1]) & (Vr <= v[2]), facecolor='gray')

plt.text(v[0], 1, 'A1 = {0}'.format(A1))
plt.text(v[2], 1, 'A2 = {0}'.format(A2))
plt.xlabel('$V_R$')
plt.ylabel('$P_R$')
plt.title('$T_R$ = 0.9')

plt.savefig('images/maxwell-eq-area-4.png')
```

```
>>> >>> >>> [<matplotlib.lines.Line2D object at 0x1ffe6e50>]
>>> >>> >>> [<matplotlib.lines.Line2D object at 0x1fd0e250>]
<matplotlib.collections.PolyCollection object at 0x1ffe6e90>
<matplotlib.collections.PolyCollection object at 0x1ffeae90>
>>> <matplotlib.text.Text object at 0x1ffed290>
<matplotlib.text.Text object at 0x1ffed3d0>
<matplotlib.text.Text object at 0x200eb310>
<matplotlib.text.Text object at 0x1ffc1250>
<matplotlib.text.Text object at 0x1ffceb10>
```



13.14 Constrained minimization to find equilibrium compositions

adapated from Chemical Reactor analysis and design fundamentals, Rawlings and Ekerdt, appendix A.2.3.

Matlab post

The equilibrium composition of a reaction is the one that minimizes the total Gibbs free energy. The Gibbs free energy of a reacting ideal gas mixture depends on the mole fractions of each species, which are determined by the initial mole fractions of each species, the extent of reactions that convert each species, and the equilibrium constants.

Reaction 1: $I + B \rightleftharpoons P1$

Reaction 2: $I + B \rightleftharpoons P2$

Here we define the Gibbs free energy of the mixture as a function of the reaction extents.

```
import numpy as np

def gibbs(E):
    'function defining Gibbs free energy as a function of reaction extents'
    e1 = E[0]
    e2 = E[1]
    # known equilibrium constants and initial amounts
    K1 = 108; K2 = 284; P = 2.5;
    yI0 = 0.5; yB0 = 0.5; yP10 = 0.0; yP20 = 0.0;
    # compute mole fractions
    d = 1 - e1 - e2;
    yI = (yI0 - e1 - e2) / d;
    yB = (yB0 - e1 - e2) / d;
```

```
    yP1 = (yP10 + e1) / d;
    yP2 = (yP20 + e2) / d;
    G = (-(e1 * np.log(K1) + e2 * np.log(K2)) +
         d * np.log(P) + yI * d * np.log(yI) +
         yB * d * np.log(yB) + yP1 * d * np.log(yP1) + yP2 * d * np.log(yP2))
    return G
```

The equilibrium constants for these reactions are known, and we seek to find the equilibrium reaction extents so we can determine equilibrium compositions. The equilibrium reaction extents are those that minimize the Gibbs free energy. We have the following constraints, written in standard less than or equal to form:

$-\epsilon_1 \leq 0$

$-\epsilon_2 \leq 0$

$\epsilon_1 + \epsilon_2 \leq 0.5$

In Matlab we express this in matrix form as Ax=b where $A = \begin{bmatrix} -1 & 0 \\ 0 & -1 \\ 1 & 1 \end{bmatrix}$ and $b = \begin{bmatrix} 0 \\ 0 \\ 0.5 \end{bmatrix}$

Unlike in Matlab, in python we construct the inequality constraints as functions that are greater than or equal to zero when the constraint is met.

```
def constraint1(E):
    e1 = E[0]
    return e1

def constraint2(E):
    e2 = E[1]
    return e2

def constraint3(E):
    e1 = E[0]
    e2 = E[1]
    return 0.5 - (e1 + e2)
```

Now, we minimize.

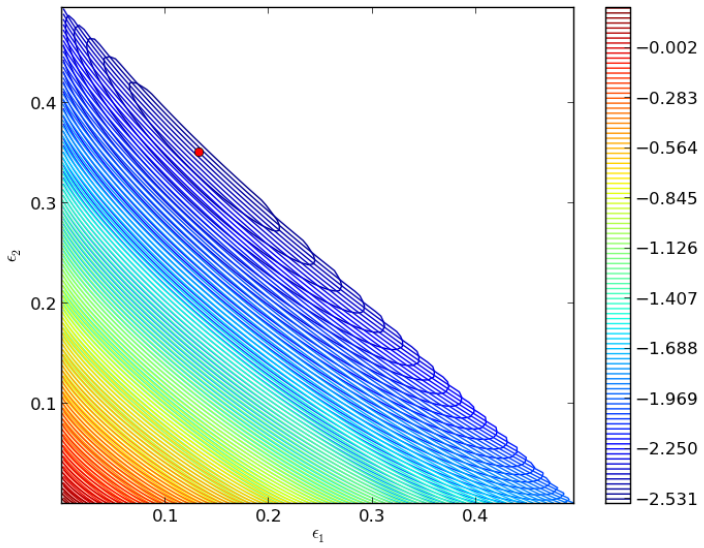
```
from scipy.optimize import fmin_slsqp

X0 = [0.133, 0.351]
X = fmin_slsqp(gibbs, X0, ieqcons=[constraint1, constraint2, constraint3])
print X

print gibbs(X)
```

```
>>> >>> Optimization terminated successfully.    (Exit mode 0)
            Current function value: -2.55942338611
            Iterations: 1
            Function evaluations: 8
```

```
            Gradient evaluations: 1
[ 0.1330313   0.35101555]
>>> -2.55942338611
```

One way we can verify our solution is to plot the gibbs function and see where the minimum is, and whether there is more than one minimum. We start by making grids over the range of 0 to 0.5. Note we actually start slightly above zero because at zero there are some numerical imaginary elements of the gibbs function or it is numerically not defined since there are logs of zero there. We also set all elements where the sum of the two extents is greater than 0.5 to near zero, since those regions violate the constraints.

```
import numpy as np
import matplotlib.pyplot as plt

def gibbs(E):
    'function defining Gibbs free energy as a function of reaction extents'
    e1 = E[0]
    e2 = E[1]
    # known equilibrium constants and initial amounts
    K1 = 108; K2 = 284; P = 2.5;
    yI0 = 0.5; yB0 = 0.5; yP10 = 0.0; yP20 = 0.0;
    # compute mole fractions
    d = 1 - e1 - e2;
    yI = (yI0 - e1 - e2)/d;
    yB = (yB0 - e1 - e2)/d;
    yP1 = (yP10 + e1)/d;
    yP2 = (yP20 + e2)/d;
    G = (-(e1 * np.log(K1) + e2 * np.log(K2)) +
         d * np.log(P) + yI * d * np.log(yI) +
         yB * d * np.log(yB) + yP1 * d * np.log(yP1) + yP2 * d * np.log(yP2))
    return G


a = np.linspace(0.001, 0.5, 100)
E1, E2 = np.meshgrid(a,a)

sumE = E1 + E2
E1[sumE >= 0.5] = 0.00001
E2[sumE >= 0.5] = 0.00001

# now evaluate gibbs
G = np.zeros(E1.shape)
m,n = E1.shape

G = gibbs([E1, E2])

CS = plt.contour(E1, E2, G, levels=np.linspace(G.min(),G.max(),100))
plt.xlabel('$\epsilon_1$')
plt.ylabel('$\epsilon_2$')
plt.colorbar()

plt.plot([ 0.1330313],   [0.35101555], 'ro')

plt.savefig('images/gibbs-minimization-1.png')
plt.show()
```



You can see we found the minimum. We can compute the mole fractions pretty easily.

```
e1 = X[0];
e2 = X[1];

yI0 = 0.5; yB0 = 0.5; yP10 = 0; yP20 = 0; #initial mole fractions

d = 1 - e1 - e2;
yI = (yI0 - e1 - e2)/d;
yB = (yB0 - e1 - e2)/d;
yP1 = (yP10 + e1)/d;
yP2 = (yP20 + e2)/d;

print('y_I = {0:1.3f} y_B = {1:1.3f} y_P1 = {2:1.3f} y_P2 = {3:1.3f}'.format(yI,yB,yP1,yP2))
```

```
>>> >>> >>> >>> >>> >>> >>> >>> >>> >>> y_I = 0.031 y_B = 0.031 y_P1 = 0.258 y_P2 = 0.680
```

13.14.1 summary

I found setting up the constraints in this example to be more confusing than the Matlab syntax.

13.15 Time dependent concentration in a first order reversible reaction in a batch reactor.

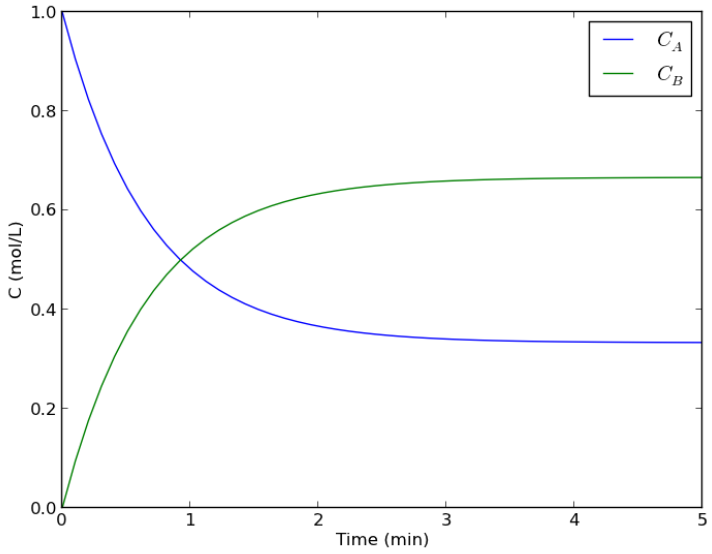
Matlab post

Given this reaction $A \rightleftharpoons B$, with these rate laws:
forward rate law: $-r_a = k_1 C_A$

backward rate law: $-r_b = k_{-1} C_B$

plot the concentration of A vs. time. This example illustrates a set of coupled first order ODES.

```
from scipy.integrate import odeint
import numpy as np

def myode(C, t):
    # ra = -k1*Ca
    # rb = -k_1*Cb
    # net rate for production of A:  ra - rb
    # net rate for production of B: -ra + rb

    k1 = 1   # 1/min;
    k_1 = 0.5   # 1/min;

    Ca = C[0]
    Cb = C[1]

    ra = -k1 * Ca
    rb = -k_1 * Cb

    dCadt =  ra - rb
    dCbdt = -ra + rb

    dCdt = [dCadt, dCbdt]
    return dCdt

tspan = np.linspace(0, 5)

init = [1, 0]  # mol/L
C = odeint(myode, init, tspan)

Ca = C[:,0]
Cb = C[:,1]

import matplotlib.pyplot as plt
plt.plot(tspan, Ca, tspan, Cb)
plt.xlabel('Time (min)')
plt.ylabel('C (mol/L)')
plt.legend(['$C_A$', '$C_B$'])
plt.savefig('images/reversible-batch.png')
```



That is it. The main difference between this and Matlab is the order of arguments in odeint is different, and the ode function has differently ordered arguments.

13.16 Finding equilibrium conversion

A common problem to solve in reaction engineering is finding the equilibrium conversion.[1] A typical problem to solve is the following nonlinear equation:

$1.44 = \frac{X_e^2}{(1-X_e)^2}$

To solve this we create a function:

$f(X_e) = 0 = 1.44 - \frac{X_e^2}{(1-X_e)^2}$

and use a nonlinear solver to find the value of X_e that makes this function equal to zero. We have to provide an initial guess. Chemical intuition suggests that the solution must be between 0 and 1, and mathematical intuition suggests the solution might be near 0.5 (which would give a ratio near 1).

Here is our solution.

```
from scipy.optimize import fsolve

def func(Xe):
    z = 1.44 - (Xe**2)/(1-Xe)**2
    return z

X0 = 0.5
Xe, = fsolve(func, X0)
print('The equilibrium conversion is X = {0:1.2f}'.format(Xe))
```

[1] Then again no package does yet!

```
The equilibrium conversion is X = 0.55
```

13.16.1 Footnotes

13.17 Plug flow reactor with a pressure drop

If there is a pressure drop in a plug flow reactor, [2] there are two equations needed to determine the exit conversion: one for the conversion, and one from the pressure drop.

$$\frac{dX}{dW} = \frac{k'}{F_A 0}\left(\frac{1-X}{1+\epsilon X}\right) y \tag{18}$$

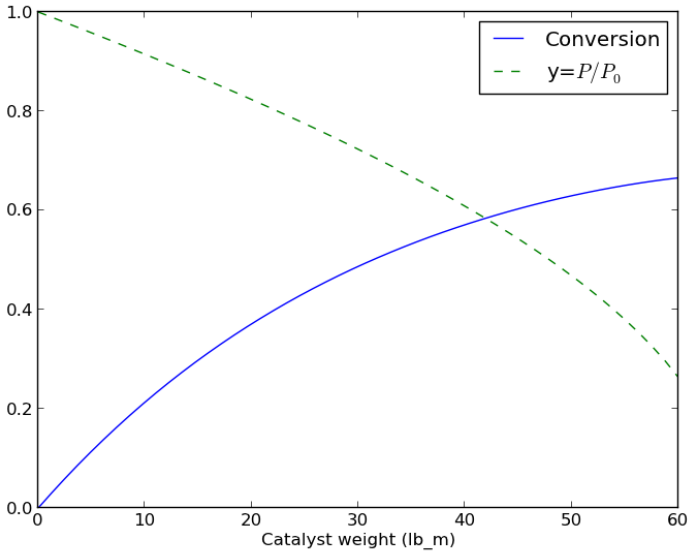
$$\frac{dX}{dy} = -\frac{\alpha(1+\epsilon X)}{2y} \tag{19}$$

Here is how to integrate these equations numerically in python.

```
import numpy as np
from scipy.integrate import odeint
import matplotlib.pyplot as plt

kprime = 0.0266
FA0 = 1.08
alpha = 0.0166
epsilon = -0.15

def dFdW(F, W):
    'set of ODEs to integrate'
    X = F[0]
    y = F[1]
    dXdW = kprime / FA0 * (1-X) / (1 + epsilon*X) * y
    dydW = -alpha * (1 + epsilon * X) / (2 * y)
    return [dXdW, dydW]

Wspan = np.linspace(0,60)
X0 = 0.0
y0 = 1.0
F0 = [X0, y0]
sol = odeint(dFdW, F0, Wspan)

# now plot the results
plt.plot(Wspan, sol[:,0], label='Conversion')
plt.plot(Wspan, sol[:,1], 'g--', label='y=$P/P_0$')
plt.legend(loc='best')
plt.xlabel('Catalyst weight (lb_m)')
plt.savefig('images/2013-01-08-pdrop.png')
```

Here is the resulting figure.

[2] Fogler, 4th edition. page 193.



13.17.1 Footnotes

13.18 Solving CSTR design equations

Given a continuously stirred tank reactor with a volume of 66,000 dmˆ3 where the reaction $A \rightarrow B$ occurs, at a rate of $-r_A = kC_A^2$ ($k = 3$ L/mol/h), with an entering molar flow of F_A0 = 5 mol/h and a volumetric flowrate of 10 L/h, what is the exit concentration of A?

From a mole balance we know that at steady state $0 = F_{A0} - F_A + Vr_A$. That equation simply states the sum of the molar flow of A in in minus the molar flow of A out plus the molar rate A is generated is equal to zero at steady state. This is directly the equation we need to solve. We need the following relationship:

1. $F_A = v0C_A$

```
from scipy.optimize import fsolve

Fa0 = 5.0
v0 = 10.

V = 66000.0  # reactor volume L^3
k = 3.0      # rate constant L/mol/h

def func(Ca):
    "Mole balance for a CSTR. Solve this equation for func(Ca)=0"
    Fa = v0 * Ca     # exit molar flow of A
    ra = -k * Ca**2  # rate of reaction of A L/mol/h
    return Fa0 - Fa + V * ra

# CA guess that that 90 % is reacted away
```

```
CA_guess = 0.1 * Fa0 / v0
CA_sol, = fsolve(func, CA_guess)

print 'The exit concentration is {0} mol/L'.format(CA_sol)
```

```
The exit concentration is 0.005 mol/L
```

It is a little confusing why it is necessary to put a comma after the CA_sol in the fsolve command. If you do not put it there, you get brackets around the answer.

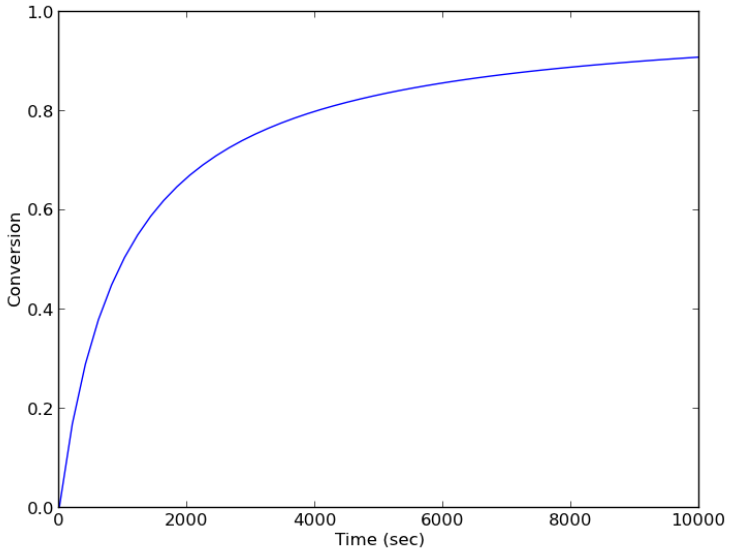
13.19 Integrating the batch reactor mole balance

An alternative approach of evaluating an integral is to integrate a differential equation. For the batch reactor, the differential equation that describes conversion as a function of time is:

$\frac{dX}{dt} = -r_A V / N_{A0}$.

Given a value of initial concentration, or volume and initial number of moles of A, we can integrate this ODE to find the conversion at some later time. We assume that $X(t = 0) = 0$. We will integrate the ODE over a time span of 0 to 10,000 seconds.

```
from scipy.integrate import odeint
import numpy as np
import matplotlib.pyplot as plt

k = 1.0e-3
Ca0 = 1.0  # mol/L

def func(X, t):
    ra = -k * (Ca0 * (1 - X))**2
    return -ra / Ca0

X0 = 0
tspan = np.linspace(0,10000)

sol = odeint(func, X0, tspan)
plt.plot(tspan,sol)
plt.xlabel('Time (sec)')
plt.ylabel('Conversion')
plt.savefig('images/2013-01-06-batch-conversion.png')
```



You can read off of this figure to find the time required to achieve a particular conversion.

13.20 Using constrained optimization to find the amount of each phase present

The problem we solve here is that we have several compounds containing Ni and Al, and a bulk mixture of a particular composition of Ni and Al. We want to know which mixture of phases will minimize the total energy. The tricky part is that the optimization is constrained because the mixture of phases must have the overall stoichiometry we want. We formulate the problem like this.

Basically, we want to minimize the function $E = \sum w_i E_i$, where w_i is the mass of phase i, and E_i is the energy per unit mass of phase i. There are some constraints to ensure conservation of mass. Let us consider the following compounds: Al, NiAl, Ni3Al, and Ni, and consider a case where the bulk composition of our alloy is 93.8% Ni and balance Al. We want to know which phases are present, and in what proportions. There are some subtleties in considering the formula and molecular weight of an alloy. We consider the formula with each species amount normalized so the fractions all add up to one. For example, Ni_3Al is represented as Ni_0.75Al_0.25, and the molecular weight is computed as 0.75*MW_Ni + 0.25*MW_Al.

We use scipy.optimize.fmin_slsqp to solve this problem, and define two equality constraint functions, and the bounds on each weight fraction.

Note: the energies in this example were computed by density functional theory at 0K.

```
import numpy as np
from scipy.optimize import fmin_slsqp

# these are atomic masses of each species
Ni = 58.693
Al = 26.982

COMPOSITIONS = ['Al', 'NiAl',              'Ni3Al',  'Ni']
MW = np.array(  [Al,  (Ni + Al)/2.0, (3*Ni + Al)/4.0, Ni])

xNi = np.array([0.0, 0.5, 0.75, 1.0])  # mole fraction of nickel in each compd
WNi = xNi*Ni / MW                      # weight fraction of Ni in each cmpd

ENERGIES = np.array([0.0, -0.7, -0.5, 0.0])

BNi = 0.938

def G(w):
    'function to minimize. w is a vector of weight fractions, ENERGIES is defined above.'
    return np.dot(w, ENERGIES)

def ec1(w):
    'conservation of Ni constraint'
    return BNi - np.dot(w, WNi)

def ec2(w):
    'weight fractions sum to one constraint'
    return 1 - np.sum(w)

w0 = np.array([0.0, 0.0, 0.5, 0.5]) # guess weight fractions

y = fmin_slsqp(G,
               w0,
               eqcons=[ec1, ec2],
               bounds=[(0,1)]*len(w0))

for ci, wi in zip(COMPOSITIONS, y):
    print '{0:8s} {1:+8.2%}'.format(ci, wi)
```

```
Optimization terminated successfully.    (Exit mode 0)
            Current function value: -0.233299644373
            Iterations: 2
            Function evaluations: 12
            Gradient evaluations: 2
Al          -0.00%
NiAl        +0.00%
Ni3Al      +46.66%
Ni         +53.34%
```

So, the sample will be about 47% *by weight* of Ni3Al, and 53% *by weight* of pure Ni.

It may be convenient to formulate this in terms of moles.

```
import numpy as np
from scipy.optimize import fmin_slsqp

COMPOSITIONS = ['Al', 'NiAl', 'Ni3Al',  'Ni']
xNi = np.array([0.0, 0.5, 0.75, 1.0])   # define this in mole fractions

ENERGIES = np.array([0.0, -0.7, -0.5, 0.0])
```

```
8
9   xNiB = 0.875  # bulk Ni composition
10
11  def G(n):
12      'function to minimize'
13      return np.dot(n, ENERGIES)
14
15  def ec1(n):
16      'conservation of Ni'
17      Ntot = np.sum(n)
18      return (Ntot * xNiB) - np.dot(n,  xNi)
19
20  def ec2(n):
21      'mole fractions sum to one'
22      return 1 - np.sum(n)
23
24  n0 = np.array([0.0, 0.0, 0.45, 0.55]) # initial guess of mole fractions
25
26  y = fmin_slsqp(G,
27                 n0,
28                 eqcons=[ec1, ec2],
29                 bounds=[(0, 1)]*(len(n0)))
30
31  for ci, xi in zip(COMPOSITIONS, y):
32      print '{0:8s} {1:+8.2%}'.format(ci, xi)
```

```
Optimization terminated successfully.    (Exit mode 0)
            Current function value: -0.25
            Iterations: 2
            Function evaluations: 12
            Gradient evaluations: 2
Al          +0.00%
NiAl        -0.00%
Ni3Al      +50.00%
Ni         +50.00%
```

This means we have a 1:1 molar ratio of Ni and Ni_0.75Al_0.25. That works out to the overall bulk composition in this particular problem.

Let us verify that these two approaches really lead to the same conclusions. On a weight basis we estimate 53.3%wt Ni and 46.7%wt Ni3Al, whereas we predict an equimolar mixture of the two phases. Below we compute the mole fraction of Ni in each case.

```
# these are atomic masses of each species
Ni = 58.693
Al = 26.982

# Molar case
# 1 mol Ni + 1 mol Ni_{0.75}Al_{0.25}
N1 = 1.0; N2 = 1.0
mol_Ni = 1.0 * N1 + 0.75 * N2
xNi = mol_Ni / (N1 + N2)
print xNi

# Mass case
M1 = 0.533; M2 = 0.467
MW1 = Ni; MW2 = 0.75*Ni + 0.25*Al

```

```
16 xNi2 = (1.0 * M1/MW1 + 0.75 * M2 / MW2) / (M1/MW1 + M2/MW2)
17 print xNi2
```

```
0.875
0.874192746385
```

You can see the overall mole fraction of Ni is practically the same in each case.

13.21 http://matlab.cheme.cmu.edu/2011/11/17/modeling-a-transient-plug-flow-reactor/

13.22 http://matlab.cheme.cmu.edu/2011/11/13/control_-cstr-m/

13.23 http://matlab.cheme.cmu.edu/2011/10/31/matlab-meets-the-steam-tables/

14 Units

14.1 http://matlab.cheme.cmu.edu/2011/08/05/using-cmu-units-in-matlab-for-basic-calculations/

14.2 Using units in python

I think an essential feature in an engineering computational environment is properly handling units and unit conversions. Mathcad supports that pretty well. I wrote a package for doing it in Matlab. Today I am going to explore units in python. Here are some of the packages that I have found which support units to some extent

1. http://pypi.python.org/pypi/units/
2. http://packages.python.org/quantities/user/tutorial.html
3. http://dirac.cnrs-orleans.fr/ScientificPython/ScientificPythonManual/Scientific.Physics.PhysicalQuantit module.html
4. http://home.scarlet.be/be052320/Unum.html
5. https://simtk.org/home/python_units
6. http://docs.enthought.com/scimath/units/intro.html

The last one looks most promising.

```
import numpy as np
from scimath.units.volume import liter
from scimath.units.substance import mol

q = np.array([1, 2, 3]) * mol
print q

P = q / liter
print P
```

```
[1.0*mol 2.0*mol 3.0*mol]
[1000.0*m**-3*mol 2000.0*m**-3*mol 3000.0*m**-3*mol]
```

That doesn't look too bad. It is a little clunky to have to import every unit, and it is clear the package is saving everything in SI units by default. Let us try to solve an equation.

Find the time that solves this equation.

$0.01 = C_{A0}e^{-kt}$

First we solve without units. That way we know the answer.

```
import numpy as np
from scipy.optimize import fsolve

CA0 = 1.0  # mol/L
CA = 0.01  # mol/L
k = 1.0    # 1/s

def func(t):
    z = CA - CA0 * np.exp(-k*t)
    return z

t0 = 2.3

t, = fsolve(func, t0)
print 't = {0:1.2f} seconds'.format(t)
```

```
t = 4.61 seconds
```

Now, with units. I note here that I tried the obvious thing of just importing the units, and adding them on, but the package is unable to work with floats that have units. For some functions, there must be an ndarray with units which is practically what the UnitScalar code below does.

```
import numpy as np
from scipy.optimize import fsolve
from scimath.units.volume import liter
from scimath.units.substance import mol
from scimath.units.time import second
from scimath.units.api import has_units, UnitScalar

CA0 = UnitScalar(1.0, units = mol / liter)
CA = UnitScalar(0.01, units = mol / liter)
k = UnitScalar(1.0, units = 1 / second)

@has_units(inputs="t::units=s",
           outputs="result::units=mol/liter")
def func(t):
```

```
15      z = CA - CA0 * float(np.exp(-k*t))
16      return z
17
18  t0 = UnitScalar(2.3, units = second)
19
20  t, = fsolve(func, t0)
21  print 't = {0:1.2f} seconds'.format(t)
22  print type(t)
```

```
t = 4.61 seconds
<type 'numpy.float64'>
```

This is some heavy syntax that in the end does not preserve the units. In my Matlab package, we had to "wrap" many functions like fsolve so they would preserve units. Clearly this package will need that as well. Overall, in its current implementation this package does not do what I would expect all the time.[1]

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