Final Exam

December 7, 2015

CBE 521, Fall 2014
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1 Mean Squared Displacement

The mean square displacement $\langle x^2 \rangle$ of a Brownian particle in one dimension is defined by Einstein as :

$$\langle x^2 \rangle = \int_{-\infty}^{\infty} x^2 f(x,t) dx$$

1.1 (a) Find $\langle x^2 \rangle$ if:

$$f(x,t) = \frac{e^{-\left(\frac{x^2}{4Dt}\right)}}{\sqrt{4\pi Dt}}$$

then $\langle x^2 \rangle$ is:

$$\langle x^2 \rangle = \frac{1}{\sqrt{4\pi Dt}} \int_{-\infty}^{\infty} x^2 e^{-\left(\frac{x^2}{4Dt}\right)} dx$$

In [1]:
```
from sympy import *
from sympy import exp, sqrt, pi, oo
init_printing()
from IPython.display import display

#Plotting
%matplotlib inline
import matplotlib.pyplot as plt
```

In [2]:
```
x = Symbol('x', real=True, positive=True) # position
D = Symbol('D', real=True, positive=True) # diffusion coef.
t = Symbol('t', real=True, positive=True) # time

gaussian_2 = x**2 * exp(-(x**2)/(4. * D * t))/sqrt(4 * pi * D * t)
integrate(gaussian_2, (x,-oo,oo), conds = 'none')
```

Out[2]:

$$2.0Dt$$

A Gaussian function describes the the position (random walk) of a particle, and by integrating over all possible locations, the intuitive result of 2Dt is obtained.

1.2 (b) Show that the mean displacement is:

$$\langle x\rangle = \int_{-\infty}^{\infty} xf(x,t)dx = 0$$

The probability distribution function for a particle in one demension may be found by solving the one-dimensional diffusion equation:

$$\frac{\partial f(x,t)}{\partial t} = D\frac{\partial^2 f(x,t)}{\partial x^2}$$

Where the probability distribution function is $f(x,t)$. The probability distribution function for the location of a particle is obtained by solving the above equation and the result shows that the probability of finding the particle at x(t) is Gaussian and the width of the Gaussian distribution is time dependent. The probability distribution function is:

$$f(x,t) = \frac{e^{-\left(\frac{x^2}{4Dt}\right)}}{\sqrt{4\pi Dt}}$$

Using the probability distribution function, the mean of a given function L is written as $\langle L(x,t)\rangle$ at time t and is defined as:

$$\langle L(t)\rangle \equiv \int_{-\infty}^{\infty} L(x,t)f(x,t)dx$$

The mean squared displacement of a particle about the origin will be defined as:

$$\text{Mean Square Displacement} \equiv \langle x(t)\rangle$$

These implies that the mean displacement is Gaussian, the width of the Gaussian distribution is time dependent: $\langle x\rangle = \langle x(t)\rangle$

$$\langle x\rangle = \frac{1}{\sqrt{4\pi Dt}}\int_{-\infty}^{\infty} xe^{-\left(\frac{x^2}{4Dt}\right)}dx$$

Let

$$a = \frac{1}{4Dt} \tag{1}$$
$$b = \frac{1}{\sqrt{4\pi Dt}} \tag{2}$$
$$\langle x\rangle = b\int_{-\infty}^{\infty} xe^{-ax^2}dx \tag{3}$$
$$= b\left[-\frac{1}{2a}e^{-ax^2}\right]\Bigg|_{-\infty}^{\infty} \tag{4}$$

Which when evaluated at the integration limits of $x=\infty$ and $x=-\infty$ results in:

$$\langle x\rangle = 0 - 0 = 0$$

1.3 (c) Find particle displacement in infinite half space

The mean displacement $\langle x\rangle$ of a Brownian particle in one dimension in infinite half space is described by:

$$\langle x\rangle = \int_0^{\infty} xf(x,t)dx$$

```
In [4]: integrate(gaussian_2, (x,0,oo), conds = 'none')
```

Out [4]:

$$1.0Dt$$

A Gaussian function describes the the position (random walk) of a particle, and by integrating over the infinite half space, the result of 1Dt is obtained.

2 Dynamic Light Scattering of Mono Dispersed Sample

A measurement of the time correlation function by Dynamic Light Scattering gave the data summarized in the table on the right. Find the effective diffusion coefficient if the wave number is q = 1.87x107. Assume that the sample is mono dispersed.

t	g^1(t)
0.000	1.000
0.001	0.498
0.002	0.248
0.003	0.124
0.004	0.061
0.005	0.030
0.006	0.015
0.007	0.008
0.008	0.004
0.009	0.002
0.010	0.001

Data will be fit to the following equation:

$$g^1(q,t) = exp\left(-q^2\bar{D}t\right)$$

Where $\bar{D}$ is the effective diffusion coeficient.

2.0.1 Write numerical routine to fit data

In [5]:
```
import numpy as np
import scipy.optimize
```

Write function to be minimized (objective function) and function for viewing the results

In [19]:
```
def objective_func(D_guess, q, t_meas, g_meas):
    Tau = q**2 * D_guess # decay rate
    g_calc = np.exp(-Tau*t_meas)
    error = (np.log(g_calc) - np.log(g_meas))# linearize the error by taking log of exponentia
    error_norm = np.linalg.norm(error)
    return error_norm

def calc_ln_g(D, q, t): # calculates the log of the accumulation function
    Tau = q**2 * D # decay rate
    ln_g = -Tau*t
    return ln_g
```

The Measured Data

In [20]:
```
t_meas = np.linspace(0, 0.01,11) #time
g_meas = np.array([1.000,0.498,0.248,0.124,0.061,0.030,0.015,
                   0.008,0.004,0.002,0.001], dtype = np.double) #measured autocorrelation data
```

Run optimization routine

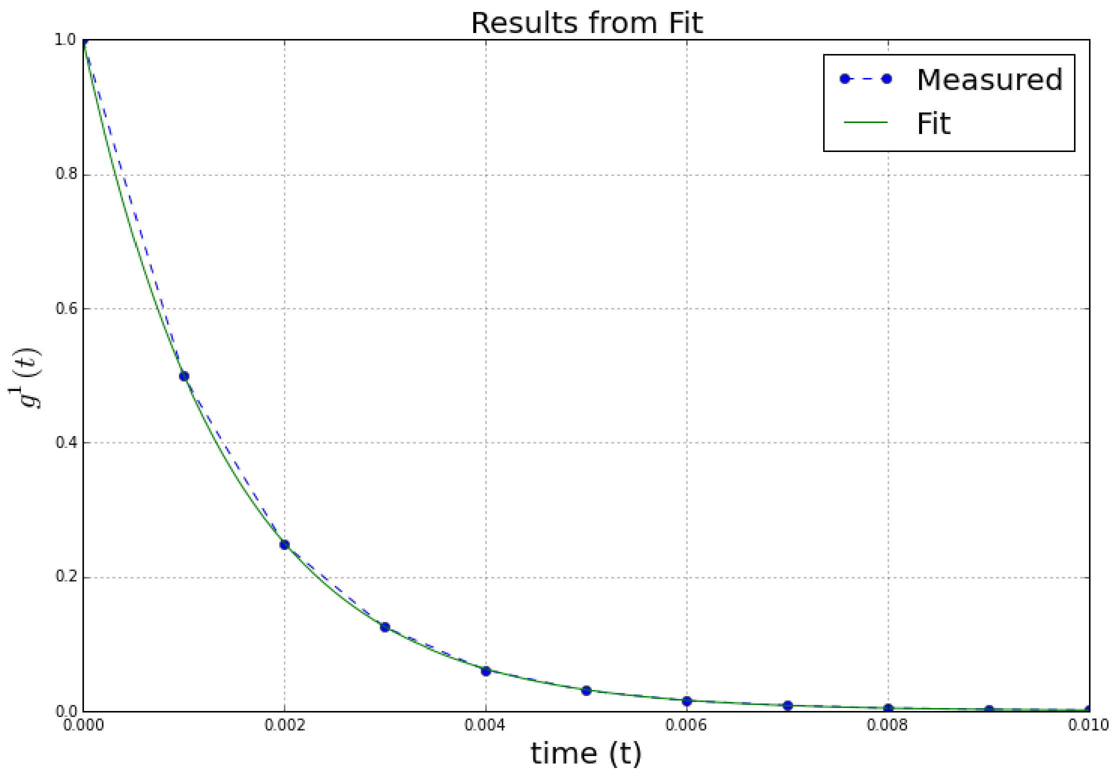
```
In [21]: ln_g_meas = np.log(g_meas) # take ln of accumulation function
         q = 1.87*10**7 # wave vector
         D_guess = 10.0**-12 # initial guess

         res = scipy.optimize.minimize(objective_func, D_guess, args=(q, t_meas, g_meas), method='Nelde
                                       options={'xtol': 1e-8, 'disp': True})
         print(res)
```

```
Optimization terminated successfully.
         Current function value: 0.078857
         Iterations: 13
         Function evaluations: 26
  status: 0
    nfev: 26
 success: True
     fun: 0.078857341595611197
       x: array([  1.98125000e-12])
 message: 'Optimization terminated successfully.'
     nit: 13
```

Plot Results of Fit

```
In [22]: D_calc = res.x[0]
         print(D_calc)

         # the calculated auto correlation function
         t_plot = np.linspace(0,0.01,101)
         g_calc = np.exp(calc_ln_g(D_calc, q, t_plot))

         fig_2, ax = plt.subplots(figsize = (12,8))
         ax.plot(t_meas, g_meas,'o--', lw=1)
         ax.plot(t_plot, g_calc, lw=1)
         ax.legend(('Measured', 'Fit'),framealpha = 1, loc=0, fontsize=20)

         ax.set_xlabel('time (t)', fontsize = 20)
         ax.set_ylabel(''r'$g^{1}(t)$', fontsize = 20)
         ax.set_title('Results from Fit' , fontsize = 20)
         ax.grid(b = True, which = 'major')
         ax.grid(b = True, which = 'major')

         fig_name = 'prob_2.pdf'
         path = '/Users/Lampe/Documents/UNM_Courses/CBE-521/Exam02/'
         fig_2.savefig(path + fig_name)
```

```
1.98125e-12
```



The fit to data resulted in a calculed effective diffusion coefficient of:

$$\bar{D} = 1.981 \times 10^{-12}$$

3 Dynamic Light Scattering of Bidispersed Sample

A measurement of the time correlation function by Dynamic Light Scattering gave the data summarized in the table on the right. Find the effective diffusion coefficient if the wave number is q = 1.87x107. Assume that the sample is bidispersed.

t	g^1(t)
0.000	1.000
0.001	0.373
0.002	0.155
0.003	0.069
0.004	0.033
0.005	0.016
0.006	0.008
0.007	0.004
0.008	0.002
0.009	0.001

Data will be fit to the following equation:

$$g^1(q,t) = \frac{1}{2}\left[exp\left(-2q^2\bar{D}_1 t\right) + exp\left(-2q^2\bar{D}_2 t\right)\right]$$

Where $\bar{D}_1$ and $\bar{D}_2$ are the effective diffusion coeficients.

3.0.2 Write a numerical routine to fit the data

Write function to be minimized (objective function) and function for viewing the results

```
In [14]: def objective_func2(D, q, t_meas, g_meas):
             D_guess1 = D[0]
             D_guess2 = D[1]
             Tau1 = q**2 * D_guess1 # decay rate
             Tau2 = q**2 * D_guess2 # decay rate
             g_calc = 0.5* (np.exp(-2*Tau1*t_meas)+np.exp(-2*Tau2*t_meas))
             error = (np.log(g_calc) - np.log(g_meas))# linearize the error by taking log of exponentia
             error_norm = np.linalg.norm(error)
             return error_norm

         def calc_ln_g2(D_1, D_2, q, t): # calculates the log of the accumulation function
             Tau1 = q**2 * D_1 # decay rate
             Tau2 = q**2 * D_2 # decay rate

             ln_2g = -Tau1*t -Tau2*t
             return ln_2g
```

The Measured Data

```
In [15]: t_meas = np.linspace(0, 0.009,10) #time
         g_meas = np.array([1.000,0.373,0.155,0.069,0.033, 0.016,
                            0.008,0.004,0.002,0.001], dtype = np.double) #measured autocorrelation data
```

Run optimization routine

```
In [16]: ln_g_meas = np.log(g_meas) # take ln of accumulation function
         q = 1.87*10**7 # wave vector
         D_guess1 = 10.0**-12 # initial guess
         D_guess2 = 10.0**-12 # initial guess

         res = scipy.optimize.minimize(objective_func2, [D_guess1, D_guess2], args=(q, t_meas, g_meas),
                                       options={'xtol': 1e-8, 'disp': True})
         print(res)
```

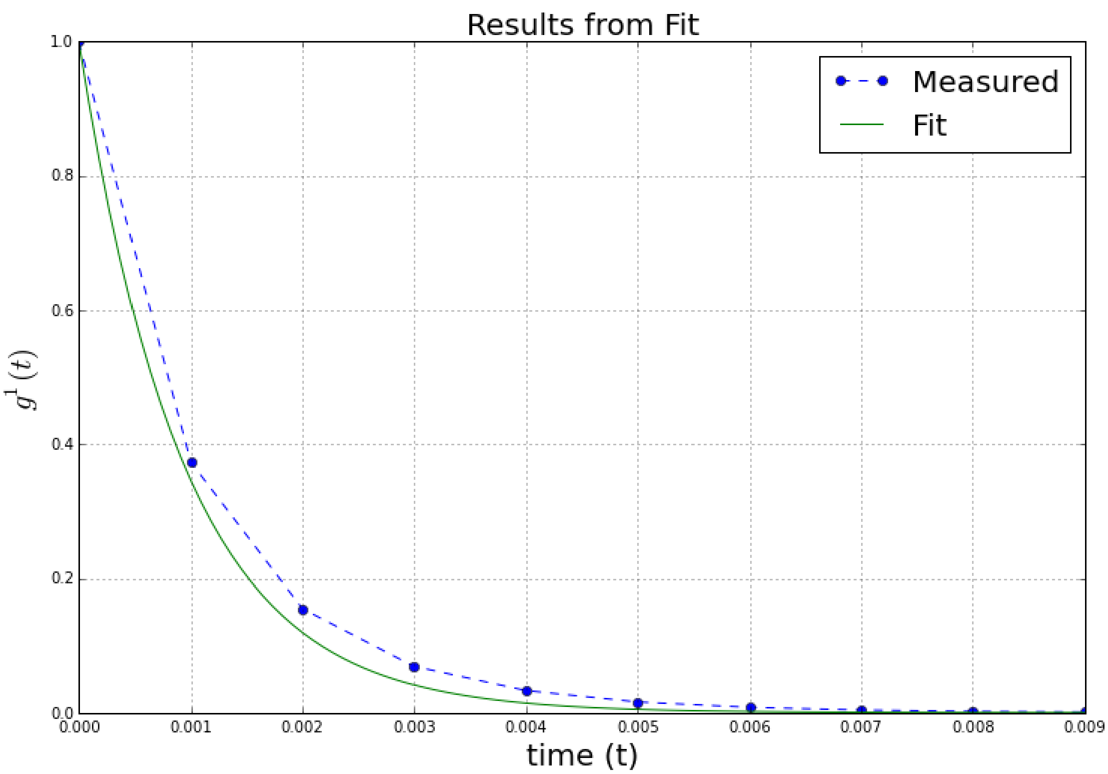
```
Optimization terminated successfully.
         Current function value: 0.019864
         Iterations: 37
         Function evaluations: 69
  status: 0
    nfev: 69
 success: True
     fun: 0.019863615028497702
       x: array([  2.04940567e-12,   9.88102622e-13])
 message: 'Optimization terminated successfully.'
     nit: 37
```

Plot Results of Fit

```
In [18]: D_calc1 = res.x[0]
         D_calc2 = res.x[1]
```

```python
print(res.x)

# the calculated auto correlation function
t_plot = np.linspace(0,0.009,100)
g_calc = np.exp(calc_ln_g2(D_calc1,D_calc2, q, t_plot))

fig_3, ax = plt.subplots(figsize = (12,8))
ax.plot(t_meas, g_meas,'o--', lw=1)
ax.plot(t_plot, g_calc, lw=1)
ax.legend(('Measured', 'Fit'),framealpha = 1, loc=0, fontsize=20)

ax.set_xlabel('time (t)', fontsize = 20)
ax.set_ylabel(''r'$g^{1}(t)$', fontsize = 20)
ax.set_title('Results from Fit' , fontsize = 20)
ax.grid(b = True, which = 'major')
ax.grid(b = True, which = 'major')

fig_name = 'prob_3.pdf'
path = '/Users/Lampe/Documents/UNM_Courses/CBE-521/Exam02/'
fig_3.savefig(path + fig_name)
```

```
[  2.04940567e-12   9.88102622e-13]
```



The fit to data resulted in a calculed effective diffusion coefficients of:

$$\bar{D}_1 = 2.049 \times 10^{-12}$$

$$\bar{D}_2 = 9.881 \times 10^{-13}$$