Final Exam Solutions
Administered: Wednesday, December 7, 2016
36 points

For each problem part: 0 points if not attempted or no work shown,
1 point for partial credit, if work is shown,
2 points for correct numerical value of solution

Problem 1. (8 points)
For many polymers it has been observed that tensile strength (TS) increases with increasing molecular weight. Mathematically, TS is a function of the number-average molecular weight, $\overline{M}_n$, according to

$$TS = TS_\infty - \frac{A}{\overline{M}_n} \qquad (1)$$

where TS_∞ is the hypothetical tensile strength at infinite molecular weight and A is a constant. [Materials Science and Engineering: An Introduction, 5th Edition, William D. Callister, John Wiley & Sons, Inc., New York, 2000, p. 480.]

For the TS vs $\overline{M}_n$ data given in the file, http://utkstair.org/clausius/docs/mse301/data/xm4p01_f16.txt, perform the following tasks.

(a) Identify all variables, $y = mx + b$, when equation (1) is linearized.
(b) Report the best value of A and TS_∞.
(c) Report the standard deviations of A and TS_∞.
(d) Report the measure of fit.

Solution

(a) Identify all variables, $y = mx + b$, when equation (1) is linearized.

$$y = TS,\ x = \frac{1}{\overline{M}_n},\ m = -A,\ b = TS_\infty$$

(b) Report the best value of A and TS_∞.
(c) Report the standard deviations of A and TS_∞.
(d) Report the measure of fit.

I wrote the following script, xm4p01_f16.m, in Matlab.

```
clear all;
format long;

M = [5    187.9981084
10    1089.60797
15    1424.643243
```

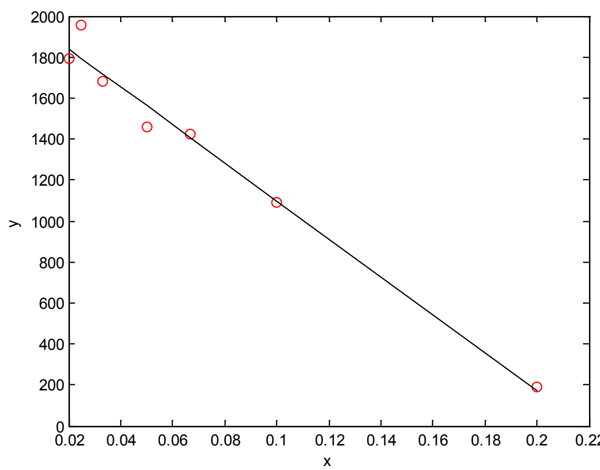
```
20     1457.308804
30     1682.800715
40     1957.433562
50     1789.973081];

n = max(size(M));
for i = 1:1:n
    x(i) = 1.0/M(i,1);
    y(i) = M(i,2);
end
[b,bsd,MOF] = linreg1(x, y)
```

At the command line prompt, I executed the script.

```
>> xm4p01_f16
```

This generated the following output.

```
b =   1.0e+03 *
   2.024633376086703
  -9.257915452943271

bsd =   1.0e+02 *
   0.542914777847655
   5.909604243182518

MOF =   0.980033528920562
```



Thus

(b) Report the best value of A and TS_∞.

$$TS_\infty = 2025 \ MPa$$

$$A = 9258 \ MPa \cdot kDa$$

(c) Report the standard deviations of A and TS_∞.

$$\sigma_{TS_\infty} = 54.3 \ MPa$$

$$\sigma_A = 591 \ MPa \cdot kDa$$

(d) Report the measure of fit.

MOF = 0.98

Problem 2. (12 points)
We are testing a polymer membrane designed to catalytically filter microbes. The concentration of microbe *A*, $C_{A,0}$, on one side of the membrane, located at *z* = 0, is $C_{A,0}$. The gradient of the microbe concentration on the same side of the membrane is $\left.\frac{dC_A}{dz}\right|_0$. Inside the polymer membrane, a chemical agent kills the microbe. The following equation describes the profile of the microbe concentration within the membrane,

$$0 = D\frac{d^2C_A}{dz^2} - k\sqrt{C_A}$$

Answer the following questions.

(a) Is this ODE problem linear or nonlinear?
(b) Is this ODE problem an initial value problem or a boundary value problem?
(c) Convert this second order ODE into a system of two first order ODEs.
(d) For a membrane of thickness, *L* = 5 cm, and the following numerical values, $D = 1.0 \cdot 10^{-6}\,\frac{cm^2}{s}$, $k = 2.8 \cdot 10^{-9}\,\frac{\left(\frac{mol}{\ell}\right)^{1/2}}{s}$, $C_{A,0} = 1.0 \cdot 10^{-2}\,\frac{mol}{\ell}$ and $\left.\frac{dC_A}{dz}\right|_0 = -2.5 \cdot 10^{-3}\,\frac{mol}{\ell \cdot cm}$, find the concentration of the microbe on the far side of the membrane.
(e) For the conditions in part (d) sketch the concentration profile.
(f) For the conditions in part (d), verify that your discretization resolution was sufficient.

Solution

(a) Is this ODE problem linear or nonlinear?

The problem is nonlinear due to the presence of the square root of the concentration.

(b) Is this ODE problem an initial value problem or a boundary value problem?

This problem is an initial value problem because both conditions are given at the same value of the independent variable, *z*.

(c) Convert this second order ODE into a system of two first order ODEs.

This conversion follows a three step process.

Step 1. Define new variables.

$$y_1 = C_A \qquad\qquad y_2 = \frac{dC_A}{dz}$$

Step 2. Write ODEs for the new variables.

$$\frac{dy_1}{dz} = y_2 \qquad \frac{dy_2}{dz} = \frac{k}{D}\sqrt{y_1} \quad \left(\text{from } 0 = D\frac{dy_2}{dz} - k\sqrt{y_1}\right)$$

Step 3. Write initial conditions for the new variables.

$$y_1(z=0) = C_{A,0} \qquad y_2(z=0) = \left.\frac{dC_A}{dz}\right|_0$$

(d) For a membrane of thickness, L = 5 cm, and the following numerical values, $D = 1.0 \cdot 10^{-6}\,\frac{cm^2}{s}$, $k = 2.8 \cdot 10^{-9}\,\frac{\left(\frac{mol}{\ell}\right)^{1/2}}{s}$, $C_{A,0} = 1.0 \cdot 10^{-2}\,\frac{mol}{\ell}$ and $\left.\frac{dC_A}{dz}\right|_0 = -2.5 \cdot 10^{-3}\,\frac{mol}{\ell \cdot cm}$, find the concentration of the microbe on the far side of the membrane.

(e) For the conditions in part (d) sketch the concentration profile.

(f) For the conditions in part (d), verify that your discretization resolution was sufficient.

I modified the input file for rk4n.m, which uses the classical fourth-order Runge-Kutta method to solve a system of n ODEs.

```
function dydx = funkeval(x,y);
D = 1.0e-6; % cm^2/s
k = 2.8e-09; % (mol/l)^(1/2)/s
dydx(1) = y(2);
dydx(2) = k/D*sqrt(y(1));
```

I wrote a little script, xm4p02_f16.m. This script sets the initial conditions and calls the Runge-Kutta method twice with n = 1000 and 10,000 intervals. If we obtain the same answer for both discretization resolution, then we know that we have a good result.

```
clear all;
format long

n = 1000;
xo = 0;
xf = 5;
CA0 = 1.0e-2; % mol/l
dCAdz0 = -2.5e-3; % mol/l/cm
yo = [CA0,dCAdz0];
[x,y]=rk4n(n,xo,xf,yo);
y_n1000 = y(n+1,1)

n = 10000;
[x,y]=rk4n(n,xo,xf,yo);
y_n10000 = y(n+1,1)
```

At the command line prompt, I executed the script, xm4p02_f16.m.

```
>> xm4p02_f16
```

This generated the following output.

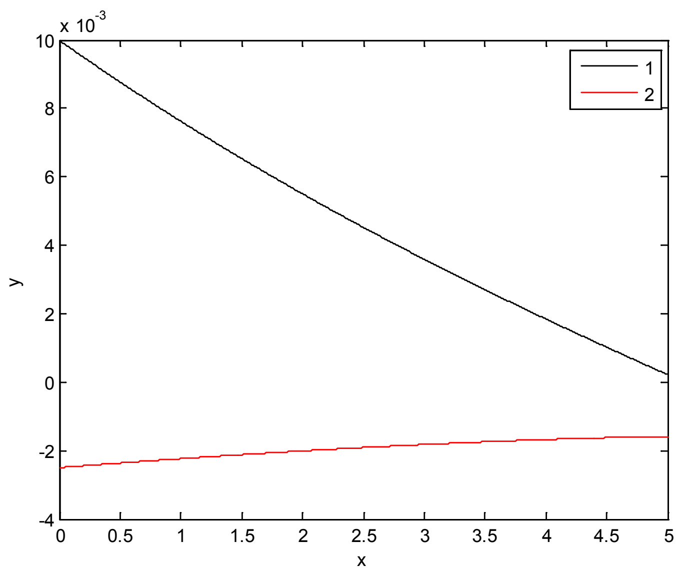
```
y_n1000 =      2.250848669161831e-04

y_n10000 =     2.250848669158090e-04
```

The two results agree, so we had a good discretization resolution.

So the concentration on the far side of the membrane is

$$C_A(z = L) = 2.25 \cdot 10^{-4} \frac{mol}{\ell}$$

A plot of the profile is shown below. The black line marked "1" is the concentration of A. The red line marked "2" is the concentration gradient.



Problem 3. (12 points)

Molecular simulations have shown that the diffusivity of oxygen in chitosan polymer films is enhanced under humid conditions. [McDonnell, M.T., Greeley, D.A., Kit, K.M., Keffer, D.J, "Molecular Dynamics Simulations of Hydration Effects on Solvation, Diffusivity, and Permeability in Chitosan/Chitin Films" J. Phys. Chem. B 120(34) 2016 pp. 8997-9010.] Consider the diffusivities of oxygen reported for several simulations at low (15%) and high (95%) relative humidity.

	15 % RH			95% Relative Humidity	
	D	D^2		D	D^2
sample	(m^2/s)	(m^2/s)^2	sample	(m^2/s)	(m^2/s)^2
1	2.66E-11	7.07E-22	1	1.91E-10	3.64E-20
2	4.46E-11	1.99E-21	2	1.14E-10	1.30E-20
3	2.60E-11	6.78E-22	3	1.31E-10	1.72E-20
4	3.61E-11	1.31E-21	4	1.12E-10	1.25E-20
5	4.73E-11	2.24E-21	5	1.26E-10	1.59E-20
6	3.39E-11	1.15E-21	6	1.15E-10	1.32E-20
7	1.60E-11	2.56E-22	7	1.30E-10	1.69E-20
sum	2.30638E-10	8.32801E-21	sum	9.187E-10	1.251E-19

(a) Compute the sample mean of the diffusivity for both RH.
(b) Compute the sample variance of the diffusivity for both RH.
(c) What PDF is appropriate for determining a confidence interval on the difference of means?
(d) Find the lower limit on a 98% confidence interval on the difference of means.
(e) Find the upper limit on a 98% confidence interval on the difference of means.
(f) Translate your result from (d) and (e) into a statement a non-statistician can understand.

Solution:

(a) Compute the sample mean of the diffusivity for both RH.

$$D_{15} = \frac{1}{7}\sum_{i=1}^{7} x_{H,i} = \frac{2.30638 \cdot 10^{-10}}{7} = 3.29 \cdot 10^{-11} \text{ m}^2/\text{s}$$

$$D_{95} = \frac{1}{7}\sum_{i=1}^{7} x_{D,i} = \frac{9.187 \cdot 10^{-10}}{7} = 1.31 \cdot 10^{-10} \text{ m}^2/\text{s}$$

(b) Compute the sample variance of the diffusivity for both RH.

$$s_{15}^2 = \frac{n\sum_{i=1}^{n} D_{15,i}^2 - \left(\sum_{i=1}^{n} D_{15,i}\right)^2}{n(n-1)} = 1.215 \cdot 10^{-22} \text{ m}^4/\text{s}^2$$

$$s_{95}^2 = \frac{n\sum_{i=1}^{n} D_{95,i}^2 - \left(\sum_{i=1}^{n} D_{95,i}\right)^2}{n(n-1)} = 7.500 \cdot 10^{-22} \text{ m}^4/\text{s}^2$$

(c) What PDF is appropriate for determining a confidence interval on the difference of means?

We must use the t-distribution to determine the confidence interval on the difference of means when the population variance is unknown.

(d) Find the lower limit on a 98% confidence interval on the difference of means.
(e) Find the upper limit on a 98% confidence interval on the difference of means.

$$\alpha = \frac{1 - C.I.}{2} = \frac{1 - 0.98}{2} = 0.01$$

$$v = \frac{\left(\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}\right)^2}{\left[\left(\frac{s_1^2}{n_1}\right)^2 \Big/ (n_1 - 1)\right] + \left[\left(\frac{s_2^2}{n_2}\right)^2 \Big/ (n_2 - 1)\right]} \quad \text{if } \sigma_1 \neq \sigma_2$$

$$v = 7.89 \approx 8$$

The limits on the t-distribution are given by

```
>> t = icdf('t',0.01,8)

t =  -2.896459447709622
```

and for the upper limit

```
>> t = icdf('t',0.99,8)

t =   2.896459447709622
```

We next insert all of these numbers into the equation for the confidence interval on the difference of means.

$$P\left[\left(\overline{X}_1 - \overline{X}_2\right) + t_\alpha \sqrt{\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}} < (\mu_1 - \mu_2) < \left(\overline{X}_1 - \overline{X}_2\right) + t_{1-\alpha} \sqrt{\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}}\right] = 1 - 2\alpha$$

$$P\left[\begin{array}{l}\left(3.29\cdot10^{-11}-1.31\cdot10^{-10}\right)+-2.8965\sqrt{\frac{1.215\cdot10^{-22}}{7}+\frac{7.500\cdot10^{-22}}{7}} \\ \quad<\left(\mu_1-\mu_2\right)<\left(3.29\cdot10^{-11}-1.31\cdot10^{-10}\right)+2.8965\sqrt{\frac{1.215\cdot10^{-22}}{7}+\frac{7.500\cdot10^{-22}}{7}}\end{array}\right]=0.98$$

$$P\left[-1.31\cdot10^{-10}<\left(\mu_1-\mu_2\right)<-6.60\cdot10^{-11}\right]=0.98$$

(f) Translate your result from (d) and (e) into a statement a non-statistician can understand.

We are 98% sure that the diffusivity of oxygen in the chitosan film at high relative humidity is between $1.31\cdot10^{-10}$ and $6.60\cdot10^{-11}$ m^2/s greater than that at low relative humidity.

Problem 4. (4 points)

The crystalline volume fraction, ϕ_c, of a polymer specimen, s, can be related to the densities of the specimen and the density of the polymer in perfectly amorphous (a) and perfectly crystalline (c) states, via

$$\phi_c = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \tag{2}$$

[Materials Science and Engineering: An Introduction, 5th Edition, William D. Callister, John Wiley & Sons, Inc., New York, 2000, p. 464.]

For a particular polymer the transparency, measured in terms of the fractional transmittance of light, f_t, is related to the crystalline volume fraction via

$$f_t(\phi_c) = c_0 + c_1\phi_c + c_2\phi_c^{\ 2} \tag{3}$$

where the coefficients, *c*, are fit to a particular polymer.

(a) For the a polymer with f_t = 0.94 and ρ_c = 1.40 g/cm^3 and ρ_a = 1.20 g/cm^3, find the density of the polymer. The coefficients for this polymer in equation (2) are c_0 = 0.1, c_1 = 17.67 and c_2 = -17.32.
(b) What is the crystalline volume fraction?

Solution:

(a) For the a polymer with f_t = 0.94 and ρ_c = 1.40 g/cm^3 and ρ_a = 1.20 g/cm^3, find the density of the polymer. The coefficients for this polymer in equation (2) are c_0 = 0.1, c_1 = 17.67 and c_2 = -17.32.
(b) What is the crystalline volume fraction?

If I substitute equation (2) into equation (3), I have one equation with one unknown.

$$f_t = c_0 + c_1\frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} + c_2\left(\frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)}\right)^2 \tag{4}$$

This is a non-linear algebraic equation with a single unknown, ρ_s,

$$f(\rho_s) = c_0 + c_1\frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} + c_2\left(\frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)}\right)^2 - f_t \tag{5}$$

I will solve $f(\rho_s) = 0$ for ρ_s using the Newton Raphson method with numerical approximations for the derivatives. I will use the code nrnd1.m I modified the input file for nrnd1.m as follows.

```
function f = funkeval(x)
rho_s = x;
rho_c = 1.40;
rho_a = 1.20;
phi_c = (rho_c*(rho_s - rho_a)) / (rho_s*(rho_c - rho_a));
c0 = 0.1;
c1 = 17.67;
c2 = -17.32;
f_t_measured = 0.94;
f_t_theory = c0 + c1*phi_c + c2*phi_c^2;
f = f_t_theory - f_t_measured;
```

I wrote a little script, xm4p04_f16.m. This script sets the initial guess and calls the Newton Raphson method twice with one guess close to the crystalline density and one guess close to the amorphous density

```
clear all;
close all;
format long;

x0 = 1.25;
[x,err] = nrnd1(x0)

rho_s = x;
rho_c = 1.40;
rho_a = 1.20;
phi_c = (rho_c*(rho_s - rho_a)) / (rho_s*(rho_c - rho_a))

x0 = 1.35;
[x,err] = nrnd1(x0)


rho_s = x;
rho_c = 1.40;
rho_a = 1.20;
phi_c = (rho_c*(rho_s - rho_a)) / (rho_s*(rho_c - rho_a))
```

At the command line prompt, I executed the script, xm4p04_f16.m.

```
>> xm4p04_f16
```

This generated the following output.

```
icount = 1 xold = 1.250000e+00 f = 2.749712e+00 df = 4.293387e+01 xnew = 1.185955e+00  err = 1.000000e+02
icount = 2 xold = 1.185955e+00 f = -2.423898e+00 df = 1.227945e+02 xnew = 1.205694e+00  err = 1.637186e-02
icount = 3 xold = 1.205694e+00 f = -2.747746e-01 df = 9.558902e+01 xnew = 1.208569e+00  err = 2.378468e-03
icount = 4 xold = 1.208569e+00 f = -5.703349e-03 df = 9.183285e+01 xnew = 1.208631e+00  err = 5.138522e-05
icount = 5 xold = 1.208631e+00 f = -8.780082e-06 df = 9.175226e+01 xnew = 1.208631e+00  err = 7.917501e-08

x =   1.208630911196526
err =     7.917501172412117e-08
phi_c =   0.049987450938080

icount = 1 xold = 1.350000e+00 f = 2.425802e+00 df = -4.268400e+01 xnew = 1.406832e+00  err = 1.000000e+02
icount = 2 xold = 1.406832e+00 f = -9.991475e-01 df = -7.626703e+01 xnew = 1.393731e+00  err = 9.399696e-03
icount = 3 xold = 1.393731e+00 f = -4.462964e-02 df = -6.929872e+01 xnew = 1.393087e+00  err = 4.622958e-04
icount = 4 xold = 1.393087e+00 f = -8.617742e-05 df = -6.894497e+01 xnew = 1.393086e+00  err = 8.972492e-07

x =   1.393085743339579
```

```
err =      8.972491903052569e-07
phi_c =    0.970220397300831
```

Because the error is beneath our tolerance of 10^{-6}, the Newton Raphson method converged for both initial guesses. There is a solution where the polymer has a density close to the amorphous density, $\rho_s = 1.209$ g/cm^3, which corresponds to a crystalline volume fraction of 0.05.

There is another solution where the polymer has a density close to the crystalline density, $\rho_s = 1.393$ g/cm^3, which corresponds to a crystalline volume fraction of 0.97.

For the purposes of this exam, either result is acceptable. Often, opacity in polymers is caused by light scattered off the interface between crystalline and amorphous domains. Thus, a highly crystalline or a highly amorphous material may be more transparent than a polymer that contains a significant component of both crystalline and amorphous domains.