CHE613A: The Structure & Rheology Of Complex Fluids
(Assignment 5)

Submitted by
Keerthi Vasan M
Roll No.: 21102023
keerthi21@iitk.ac.in
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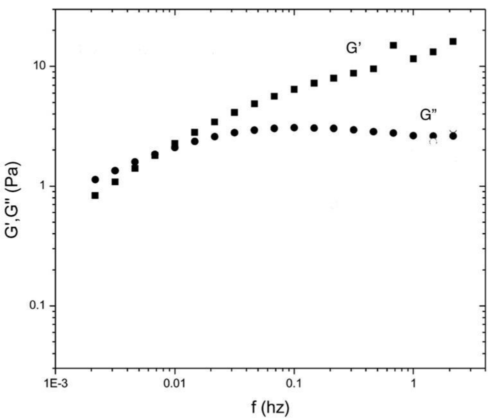
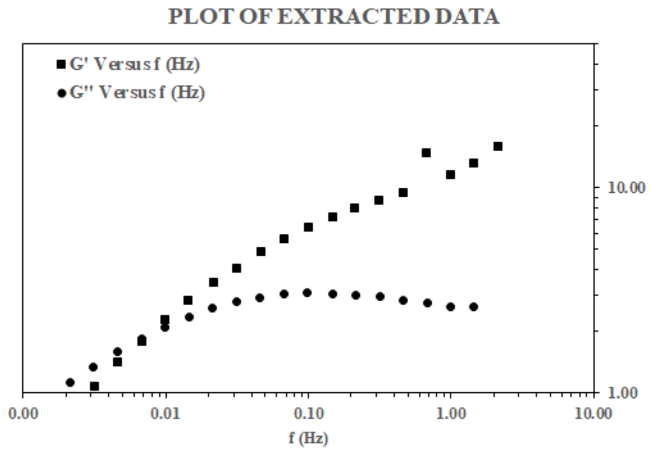
Question: Fit a multimode Maxwell model with modulus and relaxation time scales G_i and τ_i (i = 1 to N) to the given experimental plot of G' and G" versus ω. Obtain an expression for relaxation modulus G(t) and plot it with respect to time. Also calculate the shear viscosity η.

Solution: As the first part the problem the given plot is used to extract the data using the data extraction software **WebPlotDigitizer**. The given plot of G' and G" versus ω is shown below:





Now, data obtained from the **WebPlotDigitizer** is then plotted to verify the visual accuracy of the extracted data. From the above figures, it can be concluded that the extracted data reasonably fits the actual graph given in the question. Corresponding extracted data (G', G", f) are given in the table below:

f (hz)	0.0031	0.0046	0.0068	0.0099	0.0145	0.0216	0.0314	0.0462	0.0681	0.1003	0.1478	0.2122	0.3127	0.4607	0.6744	1.0000	1.4544	2.1568
G'	1.0834	1.4177	1.7969	2.2774	2.8134	3.4534	4.0792	4.8804	5.6189	6.3868	7.1673	7.9407	8.6857	9.5005	14.8752	11.5872	13.1708	15.9610
f (hz)	0.0021	0.0031	0.0046	0.0067	0.0099	0.0146	0.0213	0.0316	0.0459	0.0677	0.0990	0.1469	0.2150	0.3167	0.4607	0.6787	0.9936	1.4544
G"	1.1330	1.3469	1.6012	1.8435	2.0955	2.3515	2.5887	2.7955	2.9236	3.0382	3.0774	3.0382	2.9995	2.9424	2.8497	2.7423	2.6389	2.6389

Steps followed:

- I am using MATLAB for the this assignment 05.
- The number of Maxwell mode (N) that I am going to use is first fixed.
- Then convert the extracted frequency data (f (Hz)) into corresonding angular frequency using the relationship $\omega = 2\pi f$.
- Now, the relaxation time of the each mode is found using the relationship given to us. $\tau_i = \tau_{min} \times \left(\frac{\tau_{max}}{\tau_{min}}\right)^{\left(\frac{i=1}{N-1}\right)}$ where $i = 1, 2, 3, ...N$ and $\tau_{min} = 1/\omega_{max}$ and $\tau_{max} = 1/\omega_{min}$.
- (ω,G') data extracted from the given graph is used to find the relaxation modulus of each Maxwell mode (g$_i$ where $i = 1, 2, ...N$) using the relation $G'(\omega) = \sum_{i=1}^{N} \frac{g_i \omega^2 \tau_i^2}{1+\omega^2\tau_i^2}$.
- Now, for each mode 'i' calculate the term $\frac{\omega^2\tau_i^2}{1+\omega^2\tau_i^2}$ for different values of ω and store it as a row in a matrix variable called "abscissa". So, ith row of the matrix "abscissa" gives all the ith mode's $\frac{\omega^2\tau_i^2}{1+\omega^2\tau_i^2}$ value. Also note that, each column of any ith row of the matrix "abscissa" denotes the value of $\frac{\omega^2\tau_i^2}{1+\omega^2\tau_i^2}$ corresponding to different ω.
- Therefore, "abscissa(n,:)" denotes the entire row of the matrix "abscissa" corresponding to the mode 'n'.
- Now, using the extracted G$'(\omega)$ data and the "abscissa" matrix we can calculate the relaxation modulus of each Maxwell mode (g$_i$ where $i = 1, 2, ...N$) using the relation $G'(\omega) = \sum_{i=1}^{N} \frac{g_i \omega^2 \tau_i^2}{1+\omega^2\tau_i^2}$. For this purpose, I have used the "lsqcurvefit" Matlab function.
- Giving a initial guess value of one for relaxation modulus of each mode, "lsqcurvefit" Matlab function determines the actual relaxation time of each 'N' mode. Termination tolerance while doing the curve fitting is set at $e^{\pi/2}$ using the "options" statement of "lsqcurvefit" Matlab function.
- If any mode's relaxation modulus found is negative then the 'N' chosen is reduced and all the above procedure are repeated. Repeat the procedure till the relaxation modulus of each mode is positive.
- Once the relaxation modulus of each mode is found, it is then used to find G"(ω) data for each ω. Cross checking the ,thus found, G"(ω) with the G"(ω) that is extracted will shows accuracy of the "lsqcurvefit" fit that is done earlier to find the relaxation modulus of each mode. Plot the (ω,G"(ω)) calculated and (ω,G"(ω)) that is extracted and see how well the both plot fit each other. Change the 'N' till error in the G"(ω) calculated is minimum.
- Obtain the expression for overall relaxation modulus and shear viscosity in terms of time, relaxation modulus of each mode and relaxation time of each mode. We know that for a multimode Maxwell model $G(t) = \sum_{m=1}^{N} g_m exp\left(\frac{-t}{\tau_m}\right)$ and $\eta(t) = \sum_{m=1}^{N} \eta_m = \sum_{m=1}^{N} \tau_m G(\omega) = \sum_{m=1}^{N} g_m \tau_m exp\left(\frac{-t}{\tau_m}\right)$.

Full algorithm used in the Matlab is provided below:

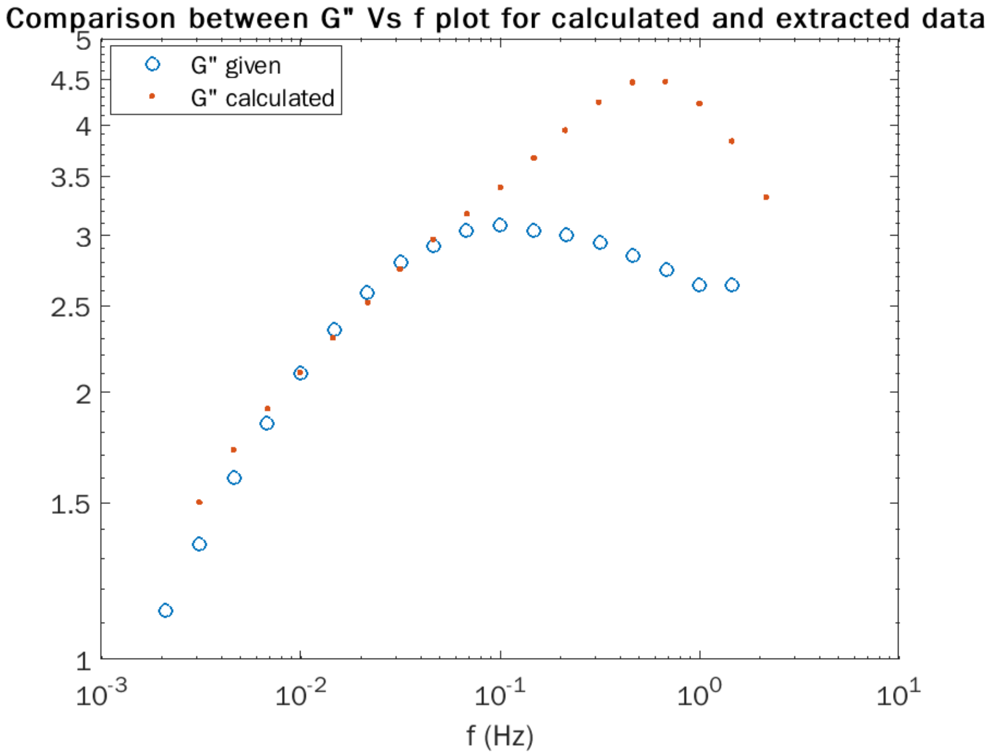
```
%-----------------------------------------

%ChE613A (The Structure and Rheology of Complex fluids)
%Assignment 05 (due date: 27/09/2021)
%Student name: Keerthi Vasan M (Roll No.: 21102023}

%-----------------------------------------


%-----------------------------------------
%Extracted data

f_prime=[0.0031 0.0046 0.0068 0.0099 0.0145 0.0216 0.0314 0.0462 0.0681 0.1003 0.1478 0.2122 0.3127 0.4607 0.6744 1.0000  1.4544 2.1568];
G_prime=[1.0834 1.4177 1.7969 2.2774 2.8134 3.4534 4.0792 4.8804 5.6189 6.3868 7.1673 7.9407 8.6857 9.5005 14.8752 11.5872 13.1708 15.9610];
f_doublePgiven=[0.0021 0.0031 0.0046 0.0067 0.0099 0.0146 0.0213 0.0316 0.0459 0.0677 0.0990 0.1469 0.2150 0.3167 0.46067 0.6787 0.9936 1.4544];
G_doublePgiven=[1.1330 1.3469 1.6012 1.8435 2.0955 2.3515 2.5887 2.7955 2.9236 3.0382 3.0774 3.0382 2.9995 2.9424 2.8497 2.7423 2.6389 2.6389];
%(f_prime,G_prime) and (f_doublePgiven,G_doublePgiven) were (f,G') and (f,G'') data respectively
%-----------------------------------------


%-----------------------------------------
%Calculation of relaxation times of the 'N' choosen Maxwell modes

N=6;
%N is number of modes in the model
%Note: If N is changed then do the corresponding change in the 'fun' statement that is used for the 'lsqcurvefit' curve fitting
Omega_prime=f_prime*2*3.14;
%Omega_prime is the angular frequency computed using the 'f' data of given (f,G') data set
n=length(Omega_prime);
%n is the number of data points present in the given (f vs G',G'') plot
omega_doublePgiven=f_doublePgiven*2*3.14;
%Omega_doublePgiven is the angular frequency computed using the 'f' data of given (f,G'') data set
Tau_max=power(Omega_prime(1),-1);
Tau_min=power(Omega_prime(n),-1);
%[Tau_min,Tau_max] is the the range within which all relaxation times will lie
%Tau_min=1/Omega_prime_max and Tau_max=1/Omega_prime_min
%Omega_prime_max = Omega_prime(n) and Omega_prime_min = Omega_prime(1)
for i=1:N
    Tau(i)=Tau_min*power((Tau_max/Tau_min),((i-1)/(N-1)));
end
%Tau is the relaxtion time of a Maxwell mode, here Tau is a array containing relaxtion times of all 'N' modes choose
%-----------------------------------------


%-----------------------------------------
%Calculation of relaxation modulus (g) of the choosen 'N' modes using the extracted storage modulus (G')
for i=1:N
    x0(i)=1;%x0 is array containing the initial points for the variables that 'fun' accepts
    for j=1:n
        abscissa(i,j)=power((Omega_prime(j)*Tau(i)),2)/(1+power((Omega_prime(j)*Tau(i)),2));
    end
end
```

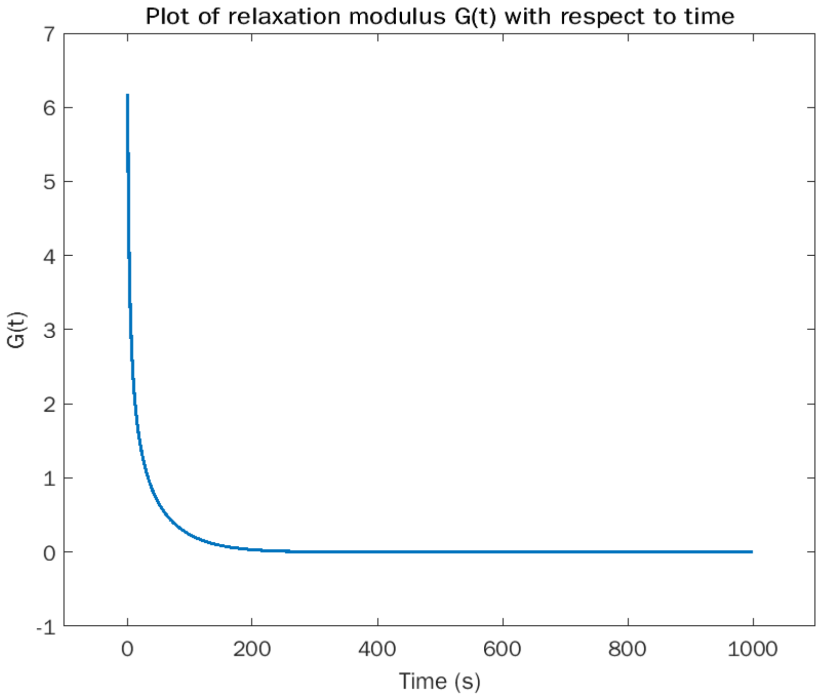
```
%abscissa is a array of (N*n) dimension and it is the input data (xdata) for the 'lsqcurvefit'
options = optimoptions('lsqcurvefit','StepTolerance',exp(pi/2));
%Above statement fixes the termination tolerence on 'abscissa' as 'exp(pi/2)
lb = [];
ub = [];
%'lb and 'ub' are vectors of lower and upper bounds respectively
fun=@(x,abscissa)(x(1)*abscissa(1,:))+(x(2)*abscissa(2,:))+(x(3)*abscissa(3,:))+(x(4)*abscissa(4,:))+(x(5)*abscissa(5,:))+(x(6)*abscissa(6,:));
%Note: If N is changed then do the corresponding change in the 'fun' statement that is used for the 'lsqcurvefit' curve fitting
g=lsqcurvefit(fun,x0,abscissa,G_prime,lb,ub,options);
%g is a array containing relaxation modulus of all the 'N' modes choosen.

%Now, we are calculating the relaxation modulus (G(t)) at very time 't'
G=0;
t=1:1000;
for i=1:N
    G=G+(g(i)*exp(-t/Tau(i)) );
end
%------------------------------------------



%------------------------------------------
%Verifying the results by using relaxation modulus (g) obtained to calculate loss modulus (G'')
sum=0;
for i=1:n
    for j=1:N
        sum=sum+((g(j)*Omega_prime(i)*Tau(j))/(1+power((Omega_prime(i)*Tau(j)),2)));
    end
    G_doubleprime(i)=sum;%G_doubleprime is the calculated loss modulus (G'')
    sum=0;
    error(i)=abs(G_doublePgiven(i)-G_doubleprime(i))/G_doublePgiven(i);
end
Avg_error=0;
for i=1:n
    Avg_error=Avg_error+error(i);
end
Avg_error=Avg_error/n;
%------------------------------------------



%------------------------------------------
%Display of the results obtained so far
fprintf('-------------------------------------------------------------')
fprintf('\nMode no.\tRelaxation modulus\tRelaxation time (s)')
for i=1:N
    fprintf('\n   %i\t\t     %.4f\t\t     %.4f',i,g(i),Tau(i))
end
fprintf('\n-------------------------------------------------------------')

G_dis="G=";
Eta_dis="Eta=";
for i=1:N
    if i==N
        G_dis=G_dis+"{"+num2str(g(i))+"*exp(-t/"+num2str(Tau(i))+")}";
        Eta_dis=Eta_dis+"{"+num2str(g(i)*Tau(i))+"*exp(-t/"+num2str(Tau(i))+")}";
```

```
    else
        G_dis=G_dis+"{"+num2str(g(i))+"*exp(-t/"+num2str(Tau(i))+")} + ";
        Eta_dis=Eta_dis+"{"+num2str(g(i)*Tau(i))+"*exp(-t/"+num2str(Tau(i))+")} + ";
    end
end
fprintf('\nFor N = %i, Average error in the G"(ω) calculated is %.4f %%',N,Avg_error*100)
fprintf('\nRelaxation modulus is %s',G_dis)
fprintf('\nShear  viscosity is %s',Eta_dis)

figure(1);
loglog(f_doublePgiven,G_doublePgiven,'o',f_prime,G_doubleprime,'.')
title('Comparison between G" Vs f plot for calculated and extracted data ')
xlabel('f (Hz)')
legend('G" given','G" calculated')


figure(2);
plot(t,G);
title('Plot of relaxation modulus G(t) with respect to time')
xlabel('Time (s)')
ylabel('G(t)')
%------------------------------------------
```

Running the above Matlab program gives the following output:

```
Local minimum possible.
lsqcurvefit stopped because the size of the current step is less than
the value of the step size tolerance.

<stopping criteria details>
------------------------------------------------------------
Mode no.        Relaxation modulus      Relaxation time (s)
   1                 3.4829                  0.0738
   2                 5.3826                  0.2734
   3                 2.8380                  1.0121
   4                 2.2147                  3.7471
   5                 1.9326                  13.8736
   6                 1.5210                  51.3663
------------------------------------------------------------
For N = 6, Average error in the G"(ω) calculated is 26.6243 %
Relaxation modulus is G={3.4829*exp(-t/0.07383)} + {5.3826*exp(-t/0.27335)} + {2.838*exp(-t/1.0121)} + {2.2147*exp(-t/3.7471)} + {1.9326*exp(-t/13.8736)} + {1.521*exp(-t/51.3663)}
Shear  viscosity is Eta={0.25714*exp(-t/0.07383)} + {1.4713*exp(-t/0.27335)} + {2.8722*exp(-t/1.0121)} + {8.2987*exp(-t/3.7471)} + {26.812*exp(-t/13.8736)} + {78.1264*exp(-t/51.3663)}
```





Reason for the choice of 'N' and other observations

Following table shows the model results for various values of 'N' and its corresponding relaxation modulus and time of each 'N' modes. Average value of all the error in calculated G″(ω) is also computed for each choice of 'N'. It is calculated as $\left\{\frac{1}{n}\sum_{i=1}^{n}\left(\frac{|G"_{\text{extracted},i}(\omega)-G"_{\text{calculated},i}(\omega)|}{G"_{\text{extracted},i}(\omega)}\right)\right\}$ where 'n' is the number of data points present in the given (f vs G′,G″) plot.

N	2		3			4			
Average error % of all computed G"(ω)	104.2945		39.2427			31.2706			
Mode	1	2	1	2	3	1	2	3	4
Relaxation modulus, g_i	24.4339	5.757	12.0952	7.3449	2.5	7.7888	6.1849	3.4581	2.0537
Relaxation time (s)	0.0738	51.3663	0.0738	1.9474	51.3663	0.0738	0.6542	5.7969	51.3663

N	5					6					
Average error % of all computed G"(ω)	26.9427					26.6243					
Mode	1	2	3	4	5	1	2	3	4	5	6
Relaxation modulus, g_i	4.288	6.3312	2.5565	2.7899	1.6278	3.3144	5.6098	2.5231	2.5965	1.5966	1.6556
Relaxation time (s)	0.0738	0.3792	1.9474	10.0015	51.3663	0.0738	0.2734	1.0121	3.7471	13.8736	51.3663

N	7						
Average error % of all computed G"(ω)	30.0927						
Mode	1	2	3	4	5	6	7
Relaxation modulus, g_i	7.0761	0.0323	7.3678	-1.9004	4.8717	-0.4916	2.1058
Relaxation time (s)	0.0738	0.2198	0.6542	1.9474	5.7969	17.2559	51.3663

- As 'N' is increased starting from 2, the average error is decreasing significantly starting from 104.2945% (for N=2) to 26.6243% (for N=6). *Note:* N=7 is special case which is discussed in the upcoming points.
- Ideal 'N' to choose is the one that have least average error in the G″(ω) calculated using $G''(\omega) = \sum_{i=1}^{N} \frac{g_i \ \omega \ \tau_i}{1+\omega^2\tau_i^2}$ relation of multimode Maxwell model (where g_i $(i = 1, 2, ...N)$ are obtained by curve fitting using "lsqcurvefit").
- When N=7, some of the relaxation modulus of the modes (g_i) were negative showing that for the given plot (shown in page 1) N=7 leads to over fitting. It is better restrict N to be less than 7. Also note that the error percentage is increasing to 30.0927% (for N=7) from 26.6243% (for N=6). So, N=6 is ideal value of number of modes to be used in the model.
- When N=6, model results are as follows (also shown in page 6):

```
----------------------------------------------------------
Mode no.        Relaxation modulus    Relaxation time (s)
   1                 3.4829                0.0738
   2                 5.3826                0.2734
   3                 2.8380                1.0121
   4                 2.2147                3.7471
   5                 1.9326                13.8736
   6                 1.5210                51.3663
----------------------------------------------------------
For N = 6, Average error in the G"(ω) calculated is 26.6243 %
Relaxation modulus is G={3.4829*exp(-t/0.07383)} + {5.3826*exp(-t/0.27335)} + {2.838*exp(-t/1.0121)} + {2.2147*exp(-t/3.7471)} + {1.9326*exp(-t/13.8736)} + {1.521*exp(-t/51.3663)}
Shear  viscosity is Eta={0.25714*exp(-t/0.07383)} + {1.4713*exp(-t/0.27335)} + {2.8722*exp(-t/1.0121)} + {8.2987*exp(-t/3.7471)} + {26.812*exp(-t/13.8736)} + {78.1264*exp(-t/51.3663)}
```

Plot of overall relaxation modulus of 'N' mode Maxwell model (G(t)) versus time is shown in page 6.