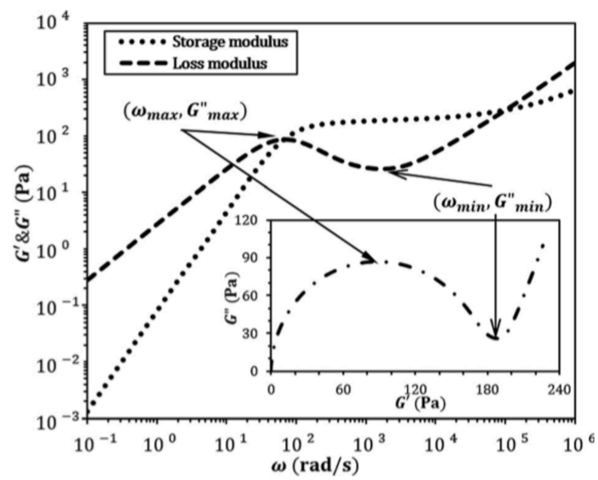
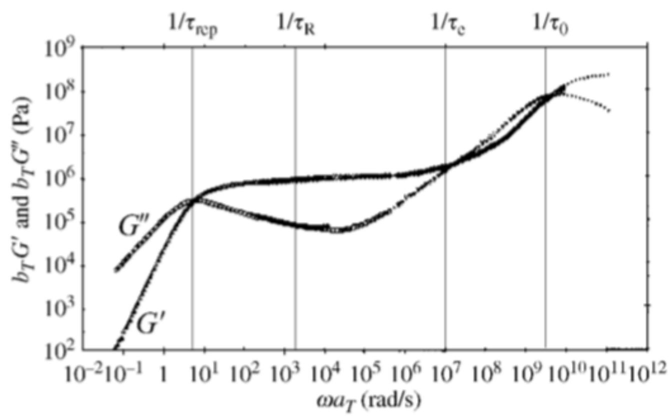
Quiz 2
Polymer Physics
January 24, 2020

Zou, Tang, Weaver, Koenig, Larson *Determination of characteristic lengths and times for wormlike micelle solutions from rheology using a mesoscopic simulation method*, J. Rheo. 59, 903 (2015) report on a new fitting program for dynamic viscoelastic data from worm-like micelles. The figure to the left shows a typical data set for worm-like micelles which is the same as the expected dynamic curve for a viscoelastic polymer (compare with figure to the right). Worm-like micelles are responsible for the vicoelastic properties of shampoo and body wash. Detergents are composed of amphiphilic molecules with one end (sodium sulfate group) hydrophilic due to ionic charging and the other end (alkane chain) hydrophobic. These molecules arrange in a sphere that can surround oily dirt with the alkane tails making the dirt water soluble. Spheres form since the charged head groups repel each other and the sphere has the widest spaced headgroups for a given volume which is governed by the length of the alkane tails. If salt is added the charge on the head groups is screened and the micelles become ellipsoidal and finally fibrous, worm-like structures tens of microns in length and nanometers in diameter. The chains are robust and can entangle.





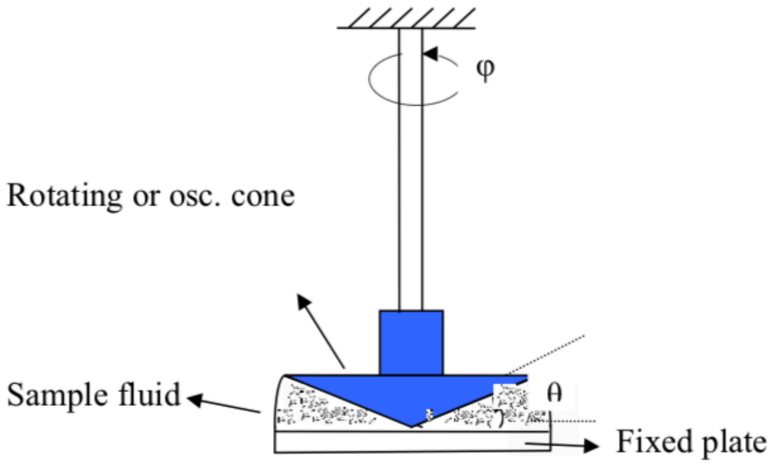
1,4-Polybutadiene From Colby, Fetters, Graessley, Macromolecules 20, 2226 (1987)

The right figure is from Colby, Fetters and Graessley and shows oscillatory viscometry data from a conventional polymer.

a) Describe the oscillatory shear measurement.
   How are G' and G'' determined?
b) What is the state of the material below the first crossover frequency or $1/\tau_{rep}$?
c) Show where the plateau modulus is and describe the state of the material in this region of frequency. What molecular weight can be determined from the plateau modulus?
d) There is a second crossover frequency at high frequency. What structure corresponds with this frequency? What is the state of the material above this second cross over frequency, above $1/\tau_e$?
e) Colby observes a third cross over frequency at $1/\tau_0$. Postulate to what you think this pertains.

ANSWERS: **Quiz 2** **Polymer Physics January 24, 2020**

a)



From https://www.uio.no/studier/emner/matnat/kjemi/nedlagte-emner/KJM3100/v07/undervisningsmateriale/Lecture%202.pdf

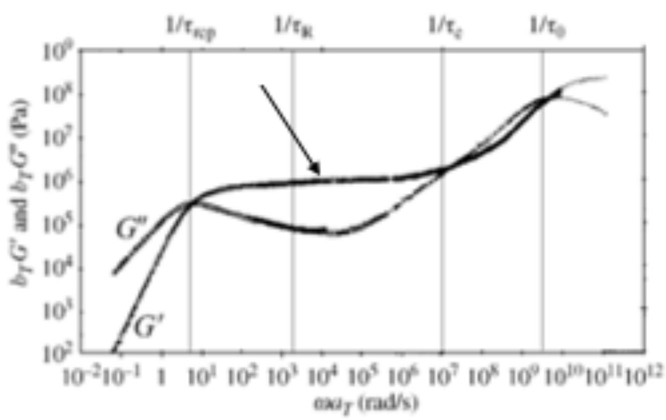
The cone is oscillated and the resulting stress is measured. Then the phase shift angle between stress and strain is determined, δ. From the complex modulus $G^*(t) = \tau_{xy}(t)/\gamma_{xy}(t)$, the storage and loss modulus are determined.

$\gamma_{xy}(t) = \gamma_o \sin \omega t$

$G^*(\omega) = G'(\omega) \sin \omega t + i\, G''(\omega) \cos(\omega t))$

b) The material is a viscous liquid since $G" > G'$. The viscosity is $G"/\omega$.

c) Plateau modulus is shown below. $G_0 = kT/M_e$ where M_e is the molecular weight between entanglements. The material in this region is rubbery.



d) The material above the second crossover is a liquid since $G" > G'$. This is for polymer within the reptation tube where there are no local constraints on the chain motion. The crossover frequency is related to the tube diameter.

e) The third cross over pertains to a transition from flow in the tube following Rouse dynamics to the persistence unit which is a one dimensional rigid structure so $G' > G"$.