Polymer Properties
Quiz 1
September 29, 2014

1) The following plot shows the behavior of melting point, $T_M$, as a function of the log of molar mass.

\[ N \sim t = \frac{2\sigma_e T_\infty}{\Delta H_f (T_\infty - T_c)} \]
\[ T_c = K_1 - \frac{K_2}{N} \]

a) Give the explanation for the shape of the melting point curve that was given in class.

b) The Hoffman-Lauritzen Equation (a.k.a. Gibbs Thompson Equation) under the assumption that the crystal thickness, $t$, is proportional to molar mass, $N$ for extended chain crystals (so $t \sim N$) yields the following dependence of crystallization temperature versus molecular weight.

Does this plot support or argue against the explanation you gave in part a? Why?
2) The Couette viscometer is composed of a cup and a bob as shown in the figure below.

![Couette viscometer diagram](image)

The bob spins with an angular velocity \( \omega \) (radians per second), and a torque \( T \) (Newton meter) is measured at point 2. The angular velocity is defined in terms of the tangential velocity, \( v(r) \) and the radius \( r \) by \( \omega = \frac{v}{r} \), and the torque is defined in terms of the force \( F(r) \) as \( T = F \cdot r \).

a) If the bob has a radius \( R \), a length of \( L \) and the gap between the bob and the cup is \( \Delta R \), write an expression for the Newtonian viscosity based on a set angular velocity \( \omega \) and a measured torque \( T \), under that assumption that \( \Delta R \ll R \).

b) For a non-Newtonian, power-law fluid the assumption that \( \Delta R \ll R \) isn’t valid since the fluid is extremely sensitive to variation in the shear rate across the gap caused by the curvature of the surfaces. How can a constant shear rate across the gap be achieved in a rotational viscometer?

c) Sketch the log of the zero shear rate viscosity versus log of shear rate for a typical polymer melt and explain what the relaxation time, \( \tau \), is from this plot.
1) a) This was explained in class as being due to a linear dependence at the low molecular weight end followed by a plateau when chain folding occurs.

b) The Hoffmann-Lauritzen equation under the assumption that $t \sim N$ is for fully extended crystals not chain folded crystals. For chain folded crystals the thickness is independent of $N$. However, the HL equation itself, seems to remove molecular weight dependence to the crystal thickness just due to the fact that $1/N$ becomes a number of low value at large $N$. This can lead to a plateau in the crystallization temperature at around 100 units even in the absence of chain folding. So the plot does not need chain folding to explain the observed behavior. So the plot of the HL equation argues against the argument given in class.

2) a) The assumption means that we ignore the curvature and treat the gap as if it were two parallel plates, so there is an assumed constant shear rate across the gap. The velocity gradient is $v(R)/\Delta R = \omega R/\Delta R$. The shear stress is $F(R)/(2\pi RL) = T/(2\pi R^3 L)$. The Newtonian viscosity is the velocity gradient divided by the shear stress, $\eta = (T\Delta R)/(2\pi R^3 L \omega)$.

b) The cone and plate viscometer achieves this since there is a constantly increasing gap in Radial position and a constantly increasing velocity with radial position. The ratio of velocity to gap is constant with radial position so the rate of strain is constant.

c) Plot of log of zero shear rate viscosity versus log of shear rate. The time constant is the inverse of the shear rate where the viscosity begins to decay.