**Polymer Properties**
**Quiz 5**
**September 26, 2014**

The local behavior (over short length scales) of a polymer can be described by three general sizes, all of which are of about the same length, 1) the Kuhn, $l_k$, or persistence length, $l_p$, 2) the packing length, p, and 3) the tube diameter, $d_t$,.

a) Describe each of these three general sizes and give a defining equation.

b) The persistence length in a polyelectrolyte depends on three size scales. List these three size scales and explain under what conditions of these three sizes you might expect to see chain charges have an affect on the persistence length.

c) The packing length is the most complex of the three general sizes that describe the local behavior of a polymer chain. How does the packing length relate to the plateau modulus? Why do you think that this relationship exists. (Use the rubber elasticity expression for the spring constant in your answer, $G_0 \sim kT/(M_e l_k^2)$).

d) The tube diameter, $d_t$, can be estimated by the specific volume per chain unit, $V_0$, and the Kuhn length, $l_k$. Use the definition of the packing length to yield a definition of p in terms of the Kuhn length and the tube diameter.

e) The tube diameter, $d_t$, relates to the loss modulus since it is used to calculate the viscosity, $\eta \sim G''/\omega$, while the packing length, p, is related to the storage modulus since it is used to calculate the plateau modulus. Define the loss and storage modulus and explain how you might expect these two phenomena, that is melt viscosity and polymer flow, and plateau modulus and static mechanical response to be independent of each other. How does your expression from part d mesh with your answer?

# ANSWERS: Polymer Properties
## Quiz 5
## September 26, 2014

1) a) Kuhn Length is the basic physical step size of the chain based on the freely jointed chain model, $<R^2> = n_k\, l_k^2$. The persistence length is based on the persistent chain model and is defined by the decay in correlation for tangent vectors $<t(s)t(0)> = \exp(-s/l_p)$. For a Gaussian chain of infinite molecular weight $2l_p = l_k$.
The packing length is a size parameter related to mechanical properties of a polymer melt or concentrated solution. It is defined by $p = NV_0/<R^2>$, where N is the number of Kuhn units of occupied volume $V_0$.
The tube diameter is the size created by entangled chains in the polymer melt or concentrated solution through which a polymer chain exists. The tube is the primitive path that the polymer chain follows through the network of entangled chains. $d_t = (V_0/l_k)^{1/2} = (m_0/(\rho\, l_k))^{1/2}$ where $m_0$ is the mass of a Kuhn unit and $\rho$ is the polymer density or concentration in a concentrated solution.

b) The three size scales are the spacing of the charges along the chain, a; the Debye screening length $\lambda_D$, and the persistence length, $l_p$. In order for charge to have an effect the separation distance, a, must be smaller than the screening length, $\lambda_D$. Also, the persistence length, $l_p$, must be larger than the charge separation distance, a, and the screening length, $\lambda_D$, must be larger than $l_p$.

c) $G_0 \sim kT/p^3 \sim kT/(M_e l_k^2)$

d) We have $p = n_k V_0/<R^2>$. $V_0 = A\, l_k = d_t^2\, l_k$, and $<R^2> = n_k\, l_k^2$, so $p = d_t^2/\, l_k$. .

e) Wiki page on dynamic modulus:

- Viscoelastic materials exhibit behavior somewhere in between that of purely viscous and purely elastic materials, exhibiting some phase lag in strain.[2]

Stress and strain in a viscoelastic material can be represented using the following expressions:

- Strain: $\varepsilon = \varepsilon_0 \sin(t\omega)$
- Stress: $\sigma = \sigma_0 \sin(t\omega + \delta)$ [2]

where

$\omega = 2\pi f$ where $f$ is frequency of strain oscillation,
$t$ is time,
$\delta$ is phase lag between stress and strain.

**Storage and loss modulus** [edit]

The storage and loss modulus in viscoelastic solids measure the stored energy, representing the elastic portion, and the energy dissipated as heat, representing the viscous portion.[2] The tensile storage and loss moduli are defined as follows:

- Storage: $E' = \frac{\sigma_0}{\varepsilon_0} \cos\delta$
- Loss: $E'' = \frac{\sigma_0}{\varepsilon_0} \sin\delta$ [2]

Similarly we also define shear storage and shear loss moduli, $G'$ and $G''$.

Complex variables can be used to express the moduli $E^*$ and $G^*$ as follows:

$$E^* = E' + iE''$$
$$G^* = G' + iG''$$ [2]

where $i$ is the imaginary unit.

The in-phase part of the modulus reflects how connected the material is, while the out of phase part of the modulus reflects how a material dissipates energy. So the two concepts differ.

From part d we have $p = d_t^2/ l_k$ so that an increase in the tube diameter directly increases the packing length. The tube diameter is independent of the Kuhn length but the packing length increases with decreasing Kuhn length. A large packing length means a large entanglement molecular weight and a weak plateau modulus. So decreasing $l_k$ leads to a weaker plateau modulus as the chain becomes more flexible. Increasing the tube diameter also leads to a weaker plateau modulus since the spacing of chains in the melt is higher, such as would occur on dilution of the polymer with a solvent. So the tube diameter reflects chain lateral packing while the packing length includes this dilution effect as well as changes in mechanical properties due to changes in chain flexibility.