

081031 Quiz 5 Morphology of Complex Materials

- 1)
 - a) Polymers display short range and long range interactions. Explain what distinguishes short- and long-range interactions.
 - b) A random walk can be constructed on a lattice by randomly selecting the direction along lattice coordinates or in free space by randomly selecting the angles for a step vector. For long walks (large n) and identical step length, l , would you expect R to results in the same value for the two simulations?
 - c) For a vector \mathbf{r}_i at chain index i on a lattice with coordination number z , the next step, \mathbf{r}_{i+1} , can occur in any direction if the choice is random including a backtrack step on the path of the chain. On average $\langle \mathbf{r}_{i+1} \rangle = 0$. If the backtrack step is forbidden the average value $\langle \mathbf{r}_{i+1} \rangle \neq 0$. Calculate this value.
 - d) What effect does the a short-range interaction of question c) have on the Kuhn step length and the chain scaling?
 - e) SJ Clark of the University of Durham says “Non-bonded interactions can be divided into two classes; short and long range interactions. Formally a force is defined to be short ranged if it decreases with distance quicker than r^{-d} where d is the dimensionality of the system (usually 3). Short ranged interactions are commonly dealt with by imposing a cut-off to the potential $V(r)$, r_c , beyond which $V(r)$ is set to 0.” (the latter being a hard core potential) Explain how these “long” and “short” range interactions relate to the “long” and “short” range interactions used in polymers. (http://cmt.dur.ac.uk/sjc/thesis_dlc/node61.html)
- 2) High molecular weight polymers are non-linear viscoelastics.
 - a) Sketch a log-log plot of viscosity versus rate of strain showing the behavior for a linearly viscous material such as water and a viscoelastic such as a high molecular weight polymer.
 - b) How does the zero shear rate viscosity of a polymer change with molecular weight?
 - c) What is the entanglement molecular weight (use your answer to b) in your answer).
 - d) What is the plateau modulus? (Is a plateau modulus displayed by a linearly viscous material such as water.)
 - e) How can the plateau modulus be used to determine the Kuhn length?
- 3) The following figure (“*Intrinsic*” and “*Topological*” Stiffness in Branched Polymers Connolly R, Bellesia G, Timoshenko EG, Kuznetsov YA Elli S, Ganazzoli F *Macromolecules* **38** 5288-5299 (2005).) shows the variation in chain persistence with chain index (from one end of the chain to the other) for simulated chains of variable local stiffness (stiffest chain is at the top with the highest persistence).

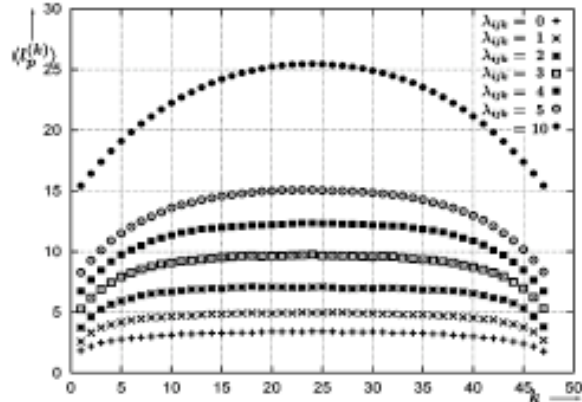


Figure 7. The persistence length plots, $\langle l_p^{(k)} \rangle$, obtained via eq 10, versus segment number, k , for various semiflexible, linear polymers, each of length 48. The strength of the intrinsic stiffness is varied between polymers by increasing the strength of the bending penalty, λ_{bse} from 0 (bottom)...5, 10 (top).

- Why would the chain persistence diminish at the ends of the chain?
- Why does the stiffest chain display the most variability in persistence along the chain?
- Persistence length is often used to describe biological molecules such as DNA which have extremely high rigidity and large persistence lengths. Based on this plot do you see any problem with the use of persistence to describe these biomolecules compared to more flexible synthetic polymers?
- How is persistence length determined by scattering?
- What result would you expect if the chain from the top curve in the plot were measured using scattering?

D a) Short range interactions occur between chain units of similar chain index. Long range interactions occur between chain units separated by a large number of chain units; well beyond the persistence length.

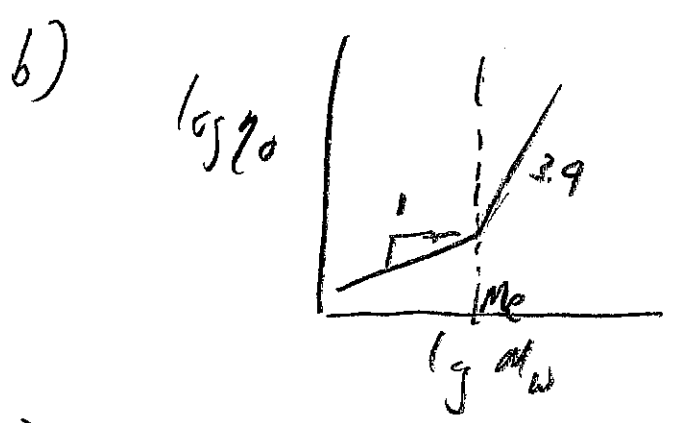
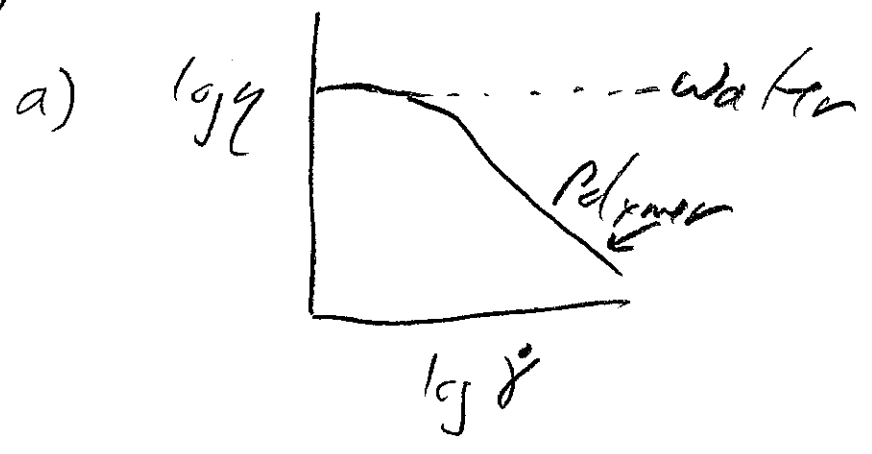
b) R would be different but it would still scale with $\langle R^2 \rangle \sim n$. The Kuhn length would vary $l_k = \frac{\langle R^2 \rangle}{n}$.

c) $\langle \underline{r}_{i+1} \rangle = 0 = \langle \underline{r}_{i+1} \rangle_{SRE} (z-1) - r_i$
 so $\langle \underline{r}_{i+1} \rangle_{SRE} = \frac{r_i}{(z-1)}$

d) It increases $l_{k, SRE} = l_k \sqrt{\frac{z}{z-2}}$
 (Chain scaling is not affected)
 $\langle R^2 \rangle \sim n$

e) Long & short range interactions for bending are not the same as long & short range interactions for polymers. Almost all polymer interactions occur over short spatial distances so they can generally be modeled with a hard core potential.

2)



c) M_c is the transition point between Rouse scaling

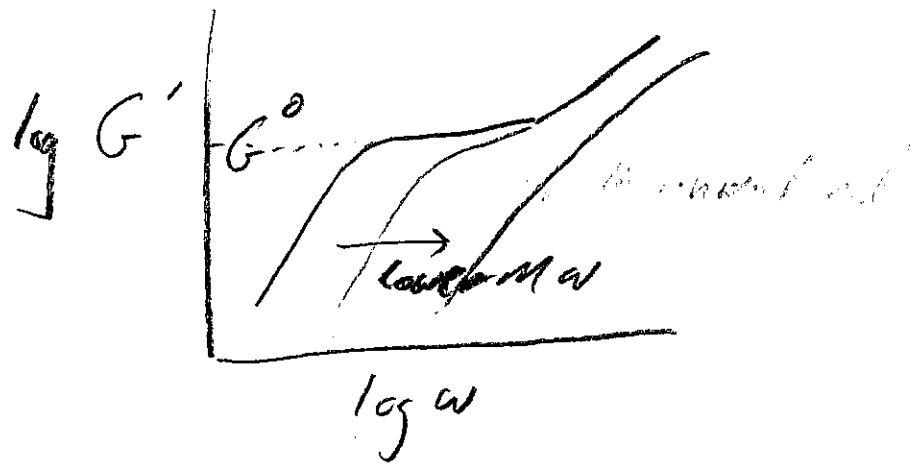
$$\eta_0 \sim M_w^1$$

& reptation scaling

$$\eta_0 \sim M_w^3 \text{ or } M_w^{2.9}$$

M_c reflects the average distance between reptation segments in a polymer and t_c .

d)



G^0 is the plateau modulus which occurs at frequencies $\omega > \frac{1}{\tau_{flow}}$ so the entanglement network dominates the storage modulus.

As the molecular weight drops the curve shifts to the right & the plateau vanishes. Water does not display G' at all since the flow is entirely viscous.

e) For single Gaussian chain (from Boltzmann Analogy)

$$E = \frac{3KT}{2nl^2} R^2$$

$$F = \frac{dE}{dR} = \left(\frac{3KT}{nl^2}\right) R \quad \text{Spring constant } k_{spring} = \frac{3KT}{nl^2}$$

For modulus $G^0 \sim n \Rightarrow Mc$

$$G^0 \sim \frac{F_{total}}{Area}$$

$$G^0 = \frac{3RT\rho}{Mc l_k}$$

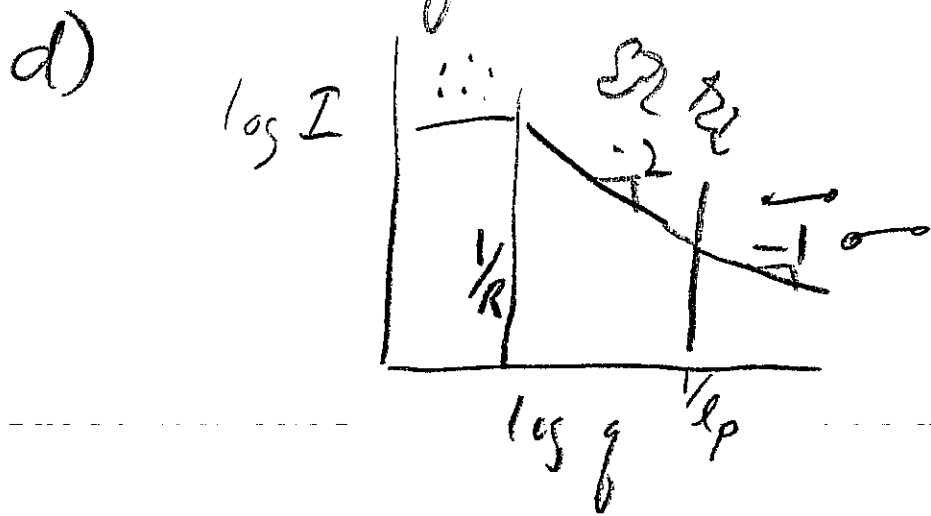
if we have ρ (density)
 T (temp) Mc ent. MW
 $\& G^0$ we can set l_k

3) a) Chains are more flexible at the ends



b) The chain end effects are greater for a stiffer chain. There are fewer Kuhn-steps for a stiffer chain, so it effectively has a lower n .

c) Chain end effects will be large for branched molecules. This means that the measured persistence will reflect an average value that may have limited relevance, it may reflect more the chain length rather than a universal feature of the molecule.



c) Would expect a smeared out distribution region + you get a molecular weight dependent persistence length.