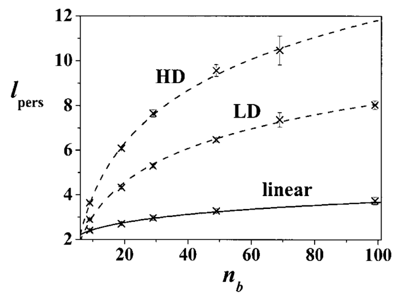
121001 Quiz 4 Polymer Properties

1) Elli et al. (*J. Chem. Phys.* **120** 6257(2004)) proposed the equation



$l_p = \left(a n_b^{\xi}\right)\left[A + B\left\{1 - \exp\left(-n_b/C\right)\right\}\right]$ to describe the functionality of persistence length with backbone molar mass for bottle brush polymers that they simulated. This equation is used to fit the data shown in the figure where HD chains have a branch on every monomer and LD chains have a branch on every other monomer (linear have no branches).

a) For the HD chains do you think that the proposed function is unique, that is, are there other functions with the same number of parameters that could fit this data? (Give an example if yes.)

b) If you were studying the molecular weight dependence of persistence length what value would you want to predict from these simulated values? Can the proposed function predict this value?

c) In class it was shown that the bottle brush simulation results follow the function $\left(\frac{1}{l_p}\right) = \left(\frac{1}{l_{p,\infty}}\right) + \left(\frac{2K}{M}\right)$ which indicates that the chain flexibility varies linearly with the number of end groups. Why do you think that flexibility is linear in the fraction of the chain composed of end groups rather than the persistence length?

2) a) Define the Debye screening length and explain how it is related to the parameter u, $u \equiv \frac{e^2}{\varepsilon a k T}$, for polyelectrolytes where a is the distance between charged groups on a polyelectrolyte chain.

b) The electrostatic persistence length can be adjusted by counter ion (salt) concentration [Dobrynin *Macromolecules* **38** 9304-14 (2005)]. Explain how counter ion concentration can have an effect on the persistence length of a polyelectrolyte.

3) a) At size scales on the order of 1 to 50 Å synthetic polymers display three structural and dynamic sizes in the melt that are used to calculate polymer properties. List these three characteristic sizes.

b) Describe the size scale associated with reptation of a chain through a tube.

c) Describe the size scale related to packing of chains in a melt.

d) Explain what the plateau modulus is, G_0.

e) How is the plateau modulus related to chain packing?

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1) a) HD has 5 data points and the proposed function has 5 free parameters so this represents the maximum number of parameters a function could have that describes this data. There are many 5 parameter functions that could equally describe this data, for instance $l_p = a + b\ n_b + c\ n_b^2 + d\ n_b^3 + e\ n_b^4$.
b) $l_{p,\infty}$, the persistence length at infinite molecular weight should be a constant value that could be obtained from this data. The proposed function at large n_b is a power-law in n_b. Such a power-law does not reach a plateau value at high n_b. The proposed function can not be used to obtain $l_{p,\infty}$.
c) Increasing the fraction of the chain composed of end groups by decreasing the molecular weight directly changes the chain flexibility. We would expect the flexibility of the chain to increase in a simple fashion with the fraction of the chain composed of end groups.

2) a) The Debye screening length is the distance beyond which the charge on a 2d surface can not be felt in the surrounding medium due to screening from counter ions. The parameter u is a similar length that corresponds to the distance from a polyelectrolyte chain where the chain charge cannot be felt due to charge screening by counter ions in a charged bilayer.

b) Dobrynin gives the expression $l_p \approx l_0 + l_p^{OSF} \approx l_0 + \frac{l_B f^2}{4(\kappa b)^2}$ (1) for the persistence length of a polyelectrolyte. The second term is the electrostatic persistence length which is proportional to the square of the fraction of charged monomers f^2, the Bjerrum length, l_B, which is the distance at which the Coulomb interaction between elementary charges equals the thermal energy, kT. It is proportional to the square of the Debye screening length κ^{-1}, the inverse of the bond length b. The concentration of counter ions is part of the Debye screening length, $\kappa^{-2} = \varepsilon kT/(4\pi ne^2)$ where n is the counter ion concentration. So the electrostatic persistence length is proportional to the inverse of the counter ion concentration.
Counter ions serve to neutralize the charge of the monomers. Counter ions condense on the chain (depending on a balance between thermal energy and the enthalpy of ionic attraction). Counter ion condensation serves to remove the charge on the polyelectrolyte chain making it behave more like an uncharged polymer chain.

3) a) Persistence or Kuhn Length; Tube Diameter (Reptation); Packing Length.
b) Chains entangle and create a restriction to motion of other chains. This restriction of other chains can be modeled as a tube. At size scales below the tube diameter the chains move with Rouse-like motion (viscosity scales with molecular weight). At larger sizes the chain is constrained, especially at relatively short times so that it can only move in the direction of the tube (viscosity is much higher than Rouse viscosity).
c) A chain in the melt occupies a volume related to its bulk density, $V_{occ} = M/\rho$. The chain also displays an end-to-end distance that scales with M, $\langle R^2\rangle = Ml^2$. By taking the ratio of these two we can remove the molecular weight dependence and calculate a size that is a characteristic of the packing of the chain in the melt. $p = V_{occ}/\langle R^2\rangle$.
d) The modulus of a polymer melt increases with frequency at low frequency (long times) following a power-law of ω^2. At long times the chain has time to be released from entanglements in the melt. At shorter times (higher frequency) the chain becomes constrained by entanglements that act as crosslinks resulting in an elastomeric response with a plateau modulus.

Across this plateau the modulus is close to constant and is related to the Gaussian modulus of a chain between crosslinks, G' ~ kT/M_e, where M_e is the entanglement molecular weight. At high frequency Rouse behavior is observed for chains between entanglements, G' ~ ω.

e) $G_0 = \frac{4\rho RT}{5M_e} = \frac{4RT}{5p^3}$ so $p \sim (M_e/\rho)^{1/3} \sim V_{occ}/\langle R^2 \rangle$ which defines an entanglement as a kind of packing constraint rather than a topological feature.