050401 Polymer Properties Quiz 1

Polymers are chain molecules comparable to chain aggregates in ceramics (such as fumed silica and pigmentary titania). Two major differences distinguish synthetic polymers from aggregates, 1) Polymers are at thermodynamic equilibrium with respect to possible chain conformations while aggregate structure is determined primarily by kinetics at the time of formation. 2) Polymer chain units ("the step") are determined by a statistical measure of persistence while aggregate units are generally spherical nano-particles.

a) A polymer in the melt is described by a Brownian model. Give a probability function that describes the probability of finding an end-to-end distance "R" for a chain of n steps of size l. What is the RMS end-to-end distance for this chain? (root-mean-square)

b) Do you expect a chain aggregate formed by collision of monomer particles with a growing aggregate to follow this Brownian model? Explain in some detail your opinion on this and include a cartoon of the growth of a chain aggregate in time. Explain the difference between a chain aggregate and a linear polymer chain in this context.

c) There are three ways to study chain structure, 1) through simulation 2) through modeling and 3) through experimental observation. Each has advantages and disadvantages and each yields different information concerning chain structure. Explain the different types of information available between a simulation of a Gaussian walk and the model of question "a". How would a simulation of aggregation in question "b" (based on your cartoon) differ from a simulation of a linear polymer chain?

d) The RMS end-to-end distance for a Gaussian polymer chain is expressed in terms of the number of chain steps (Kuhn steps) and the average length of a Kuhn step. A Kuhn step is observed as a one dimensional region in scattering or as a base unit contributing to the viscosity and diffusion of a polymer coil. Flory determined a mathematical expression for this step length, b, using the bond length, l', and the bond angle, θ'. Give this expression and explain why the step length is always larger than the length of a chemical unit such as the ethylene unit in polyethylene.

e) For a biopolymer, such as a protein, the chemical structure of the chain is more complex than the structure of a synthetic polymer such as polystyrene. Additionally, proteins are polyelectrolytes with static charges along the chain in specific locations. The combination of these two effects leads to "secondary structure" which is a specific structure for the molecule between that of the mer unit and that of the overall coil (tertiary structure of a protein). (A simple secondary structure is observed in tactic polymers as a helical coiling of the chain in crystals.) Give your opinion on the effects of secondary structure and electrostatics in proteins on the validity of chain scaling laws such as the RMS law of question "a". Also comment on the effect on the "Kuhn" length of a protein. Include a cartoon of how you think a protein chain would appear.
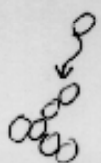
a)

1-d $\quad P_{\substack{G \\ 1-d}}(R, \sigma) = \frac{1}{\sigma \sqrt{2\pi}} \; exp\left(\frac{-1}{2}\left(\frac{R}{\sigma}\right)^2\right) dR$

3-d $\quad P_G(R, \sigma) = 4\pi R^2 \; P_{\substack{G \\ 1-d}}^3(R, \sigma) \; (3)^{3/2} dR$

$\quad\quad\quad \langle R^2 \rangle^{1/2} = n^{1/2} \ell$

b) No, aggregates are not random in a Brownian sense.

Chain Aggregate Growth by
Monomer - Cluster Aggregates

Aggregate is Branched & Structure is not
a random walk since many orientations
are blocked by growth from the outside
i.e. diffusion of monomers to the growing
aggregate. d_f should be lower than
a Brownian aggregate due to this
diffusion limited growth but higher
due to branching. $d_f \sim 1.8$ for diffusion
limited growth. $R \sim n^{\frac{1}{1.8}}$

c) Simulation of a linear Gaussian chain involves a series of randomly directed steps that are connected (i.e. sequential) making a linear chain. Simulation of aggregate growth would involve Brownian motion of a monomer which collides with an aggregate. It is most probable that collision will occur in the outer regions of the aggregate
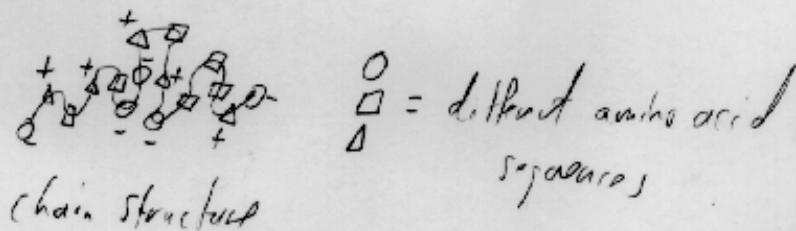

Low Probability

High Probability
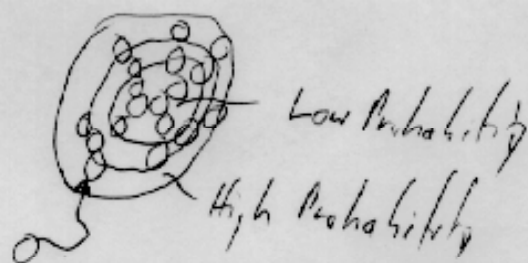
due to the growth mechanism branching is likely.
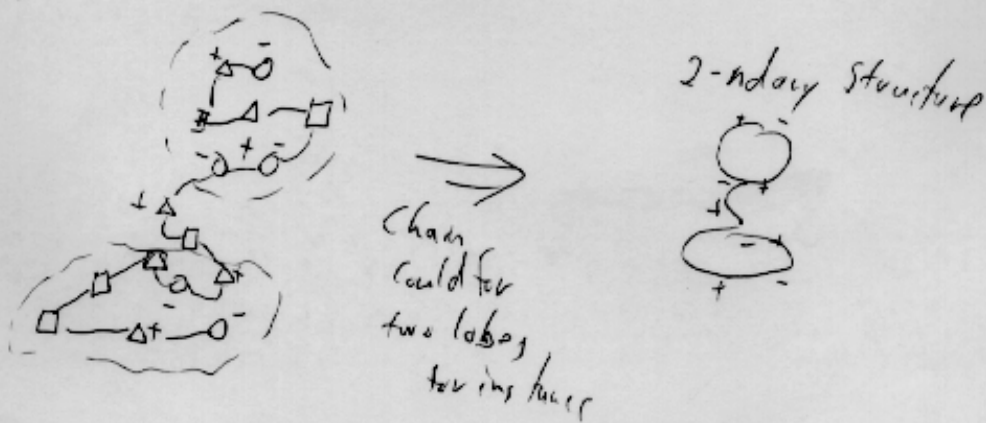
d)
$$b = \frac{\ell'}{1 - \cos \theta'}$$

b is larger than ℓ' because the bonds are not completely flexible, i.e. they have a fixed angle θ'.

e) Chain scaling won't work for proteins since the chain path is not random but follows a predictable course due to non-covalent structure and static charging

$\square = $ different amino acid sequences

chain structure

⇓

Secondary structure

Chain could fold two lobes for instance

2-ndary structure

Kuhn length has no meaning for a protein with secondary structure

A better description of primary/secondary/tertiary structure of proteins is given at http://web.mit.edu/esgbio/www/lm/proteins/structure/structure.html.