060208 Quiz 4 Morphology of Complex Materials

A linear polymer in a semi-dilute solution displays three levels of structural hierarchy: persistence level, self-avoidance scaling level (SAW) and the screened interaction level.

1) a) Explain in general terms how tacticity effects chain persistence.
   b) What is the base unit of tacticity. Define the possible states for this unit of tacticity.
   c) Why is this base unit not used to describe tacticity?
   d) Give the triad tacticity for an atactic polymer.
   e) Define heterotactic.

2) Chain scaling in dilute solutions can display only two possible states.
   a) Briefly define these two states.
   b) How can you obtain the *Gaussian*-scaling law using a derivative of a probability function?
   c) Why is a chain obeying this scaling law called a Gaussian chain? Why is it called a Brownian chain? Why is it called a random walk coil?
   d) Show how the approach of part b can be modified for a self-avoiding walk.
   e) Kohn et al.[1] have shown that many proteins in the unfolded state display SAW scaling. Explain the following plot that Kohn uses for evidence.

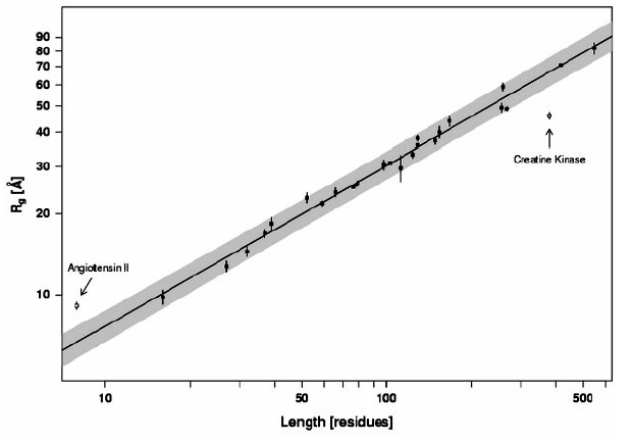


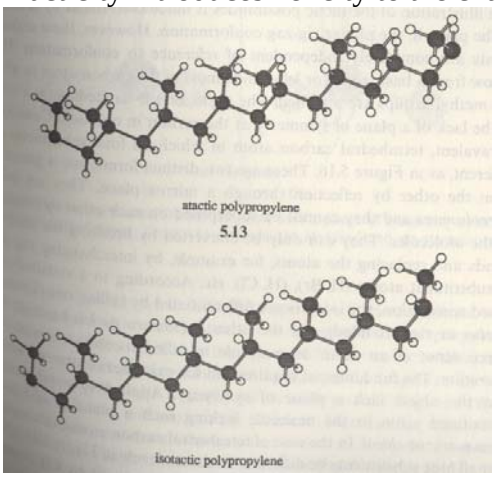
Fig. 1. The R_G of the large majority of chemically denatured proteins scale with polymer length, N, by means of the power-law relationship $R_G = R_0 N^{\nu}$. Two statistically significant outliers, creatine kinase and angiotensin II, are indicated. The solid line, which is the least-squares fit ignoring the two potential outliers, produces an exponent, $\nu = 0.598 \pm 0.028$ (95% confidence interval), that is indistinguishable from the 0.588 predicted for an excluded-volume random coil. The shaded region represents the 95% confidence intervals for future measurements, assuming that the errors about (log)R_G are normally distributed around the fitted relationship. Only the measurements for creatine kinase and angiotensin II fall outside this predictive interval, and, thus, only these measurements can be said to represent unambiguously significant deviations. Error bars indicate the reported experimental (i.e., standard) deviations of the sample. These were derived by using a variety of approaches and widely varying numbers of observations and therefore provide only an approximate indication of experimental precision.

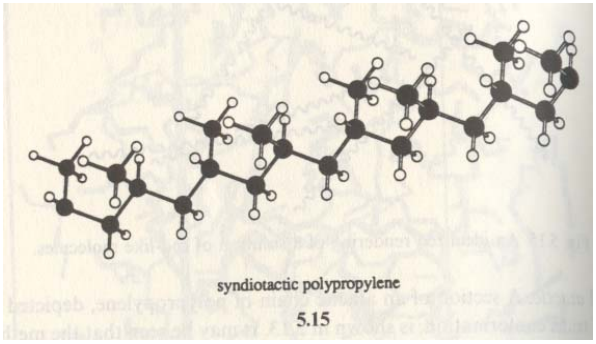
3) The concept of screening of interactions was developed by Debye for charged colloids. Debye developed the idea of a screening length that describes the distance over which interactions (such as static charge repulsion or attraction) are felt.
   a) Does the screening length increase, decrease or not change with concentration? (Explain your answer with a brief description of the nature of screening).
   b) In a polymer coil write chain scaling laws for sizes above and sizes below the screening length?
   c) Does the screening length, ξ, depend on the molecular weight of the polymer, N? Explain your answer.
   d) In the function $\xi = R_{F,SAW}\,(c/c^*)^P$ define the overlap concentration c* in terms of N, the number of persistence steps in a coil.
   e) Using the function for $R_{F,SAW}$, from (*2a*); your answer to (*3c*); and your expression for c* in (*3d*), solve for P in the expression for ξ in (*3d*).

1) Kohn JE, Millett IS, Jacob J, Zagrovic B, Dillon TM, Cingel N, Dothager RS, Siefert S, Thiyagarajan P, Sosnick TR, Hasan MZ, Pande VS, Ruczinski I, Doniach S, Plaxco KW *Random-coil behavior and the dimensions of chemically unfolded proteins. Proc. Nat. Acad. Sci.* **101** 12491-12496 (2004).

ANSWERS: 060208 Quiz 4 Morphology of Complex Materials

1) a) Tacticity introduces helicity to the chain as shown by *Paul Phillips* and Boyd below,





The interactions that lead to a regular helical structure are short range interactions and these directly control the coordination number *z*. The persistence length increases with reduction in *z* following, $b_{SRI}^2 = b^2\, z/(z\text{-}2)$.

b) The base unit of tacticity is a diad (two mer units). There are two possible states for diads, meso and racemic (m and r). Meso means that the two mer units have the same handedness, that is going along the chain the substitutions are made in the same rotational order (clockwise or counter-clockwise for instance). Racemic means that the substitutions are made in opposing rotational order.

c) NMR is the analytic technique that is sensitive to tacticity. The smallest unit of tacticity that NMR can resolve are pairs of diads or triads. A triad is composed of three mer units.

d) There are three types of triad tacticity units: *isotactic*, composed of mm triads; *syndiotactic*, composed of rr units; and *heterotactic* composed of mr and rm triads. Since there are two options to make heterotactic the distribution in a random or atactic sample has i:h:s of 25:50:25 %.

e) Heterotactic triads are composed of diads of mr and rm pairs.

2) a) Random walk state where $R \sim N^{1/2}$ b and the self-avoiding walk state (SAW) where $R \sim N^{3/5}$ b.
b) Setting the derivative with respect to the end-to-end distance R for the Gaussian probability function equal to 0 and solving for R,

$$P(R)\, dR = K\, R^2 \exp(-3R^2/(2\sigma^2))\, dR \quad \text{where } \sigma = N^{1/2}b$$

c) It is called a Gaussian chain because it is based on the Gaussian probability function. It is called a Brownian chain because it is the chain that would be obtained if the path of Brownian motion were solidified in a polymer, it is a random walk coil since it is the coil that would be obtained if a totally random walk were solidified in a linear chain.

d) The Gaussian probability function is modified by the probability of the chain not intersecting itself $p(R) = (1 - V_c/R^3)^{N\wedge 2/2} \sim \exp(-N^2V_c/(2R^3))$ for $(V_c/R^3) <<1$.

e) $\ln(R_g) = (3/5) \ln(N_{Residues})$ is the coil scaling law for a SAW chain. This might be expected for a protein in water.

3) a) Screening involves the blocking of interactions by other units of the same material (or a different material). For the case of LRI's we consider *inter*-chain interactions and *intra*-chain interactions. Increasing the concentration leads to more inter-chain interactions that block intra-chain interactions (LRI's). The blocking of interactions occurs to a greater extent at large size scales where there is a higher probability of inter-chain interference. The higher the concentration the smaller the screening length since the average separation distance between different chains becomes smaller while the average separation distance between mers in the same chain remains roughly the same.

b) Above the screening length the excluded volume is screened so the coil is Gaussian, $R \sim b_1N_1^{1/2}$. Below the screening length the chain has excluded volume so , $R \sim b_2N_2^{3/5}$. Subscripts indicate that the definition of the substructure and the number of these substructures in the chain changes with the scaling regime following renormalization of the chain.

c) The screening length, ξ, can not depend on the molecular weight since it is a size smaller than the coil size.

d) $c^* = N/R_{F,SAW}^3 = N^{-4/5}/b^3$

e) $\xi = R_{F,SAW} (c/c^*)^P = c^P N^{3/5+4P/5} b^{3P}$
so P = -3/4 since the power of N must be 0.