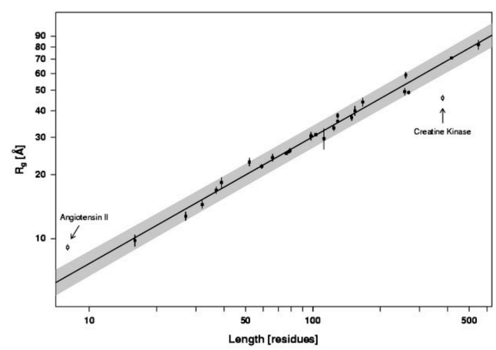
081107 Quiz 6 Morphology of Complex Materials

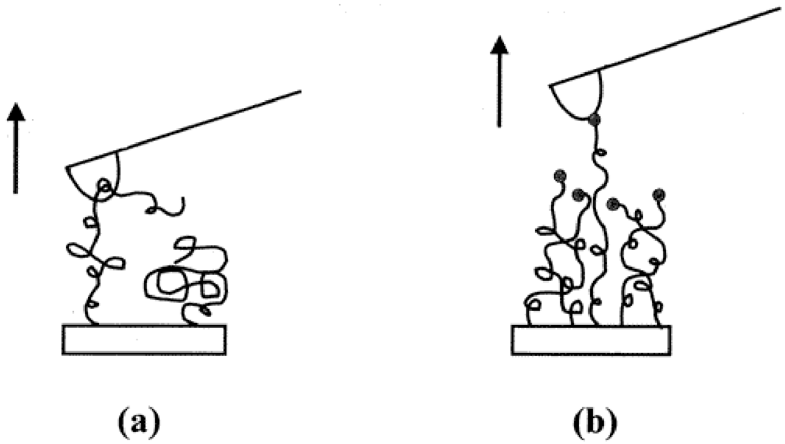
1) a) The term "Gaussian Chain" is often used to describe a polymer. Give the Gaussian function and explain what it has to do with a polymer chain. (We used a simulation to connect these in class.)
b) A polymer chain is at times described as a Brownian Chain. Explain what Brownian diffusion has to do with a polymer chain.
c) When a polymer is put in a good solvent it is called an expanded coil or a self-avoiding walk (SAW). Explain why a polymer chain expands from the Gaussian state when it is placed in solvent. (That is, what is a self-avoiding walk.)
d) How can the energy of an isolated Gaussian chain be obtained from the Gaussian Function of part a)?
e) How could this energy be used to calculate the spring constant k_{spr} for an isolated Gaussian chain, $F = k_{spr} R$.

2) The stochastic (random) tertiary structure for a polymer coil in dilute solution is described by the probability function, $P(R) = k \exp(-R^2/(n l^2))$
a) The integral of $R^2P(R)$ yields $\langle R^2 \rangle = nl^2$. Show that the derivative of this probability function yields the same scaling behavior (i.e. find the most probable size R*, maximum probability).
b) Write a similar probability function for a self-avoiding walk (SAW).
c) What is the resulting scaling function for end-to-end distance for a SAW?
d) Kohn et al. (2004 PNAS) published the following graph for a wide range of "unfolded proteins". From this plot do proteins obey stochastic hierarchies in the "unfolded" state?
e) What are the problems with this proposition?



Kohn graph shows a slope of ~0.6.

3) If a thermally equilibrated polymer chain in the Gaussian state is drawn from the ends (see picture below from *Atomic Force Microscopic Study of Stretching a Single Polymer Chain in a Polymer* Brush Yamamoto S, Tsujii Y, Fukuda T *Macromolecules* **33** 5995 - 5998 (2000)) The coil responds by modification of the structure.



a) Explain how the coil (right in "a") can be described in terms of a scaling transition when it is stretched using a tensile blob model.

b) How can you mathematically describe the size scale introduced by a pseudo-equilibrium state between the applied force F and the thermal force resulting from kT?

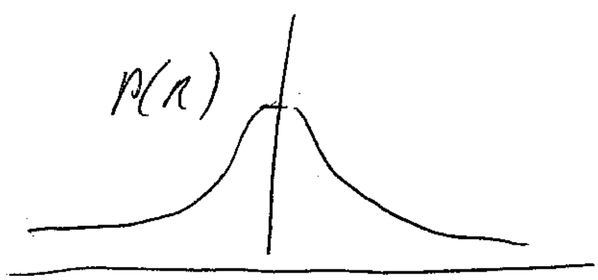
c) Sketch a log Intensity-log scattering vector (q) plot that shows how the structure responds to increasing applied force.

d) How do you expect the applied force to change if the temperature is increased?

e) Write the ideal gas law and compare the change in pressure with the change in force from part "d" with increasing temperature. Explain this comparison.

1) a) $$P(R,n) = \left(\frac{2\pi}{3} n l^2\right)^{-3/2} \exp\left[-\frac{3}{2}\frac{R^2}{nl^2}\right]$$

A polymer chain can take many conformations in time due to thermal fluctuations in bond rotation. The most probable is at end-to-end distance $R = 0$. There is a decaying probability following a Gaussian function



b) Brownian diffusion involves the random motion of a particle due to thermal diffusion driven by kT. If the diffusion path is frozen in space & we correlate time with number of steps (assuming a constant velocity) a direct analogy between the diffusion path and a random walk can be made.

c) A polymer expands due to excluded volume, that is, the walk avoids itself for large chain index differences. This restriction causes the overall chain to occupy a larger volume compared to the Gaussian state.

d) Energy of an isolated chain is obtained by comparison with the Boltzmann function,

$$P(R) = \exp\left(\frac{-E_a(R)}{kT}\right)$$

where $E_a(R)$ is the energy associated with an end-to-end distance R. This is similar to the "Energy Landscape" of a Protein. We compare with

$$P(R) \sim \exp\left(\frac{-3R^2}{2nl^2}\right)$$

yielding

$$E_a(R) = kT\left(\frac{3R^2}{2nl^2}\right)$$

e) $$\frac{dE}{dR} = F = k_{spr} R = \left(\frac{3kT}{nl^2}\right) R$$

$$\boxed{k_{spr} = \frac{3kT}{nl^2}}$$

2) a) $$\frac{d\, KR^2 \exp\left(\frac{-3R^2}{2nl^2}\right)}{dR} = \cancel{K}\left[2R \cancel{\exp\left(\frac{-3R^2}{2nl^2}\right)} - \frac{3R^2 R}{nl^2} \cancel{\exp\left(\frac{-3R^2}{2nl^2}\right)}\right] \equiv 0$$

For max

$$2 = \frac{3R^2}{nl^2} \quad \text{or} \quad \boxed{\langle R\rangle^2 \simeq \frac{2}{3} nl^2}$$

b) $$P_{SAW}(R) = k \exp\left[\frac{-3R^2}{2nl^2} - \frac{n^2 V_c}{2}\frac{}{R^3}\right]$$

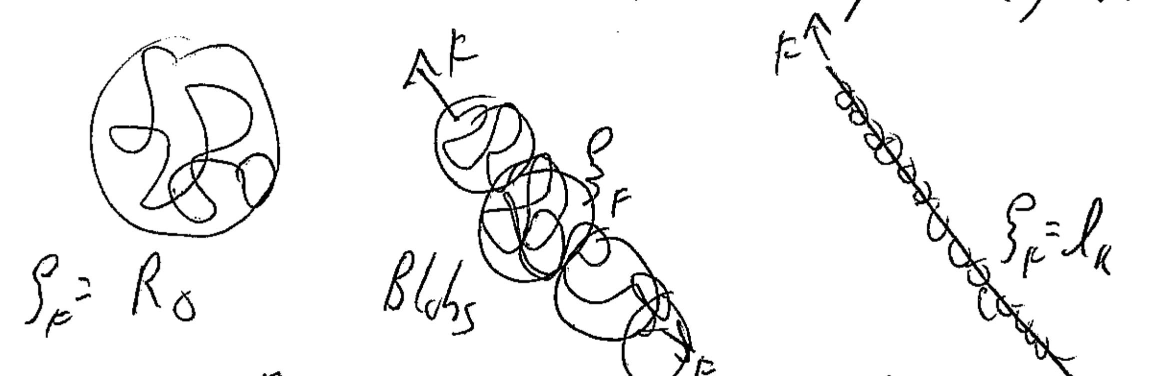
c) $\langle R^2\rangle^{1/2} \sim n^{3/5} l$

d) Log log plot with slope of $0.6 \sim 3/5$

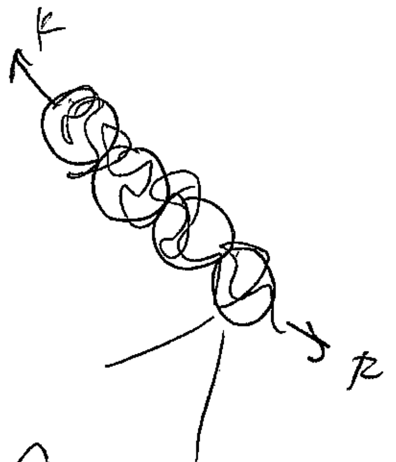
means
$$\langle R_g\rangle \sim n^{3/5} l$$
same as "c)" so chains are SAW's

e) He looks at a series of chains not a single chain. We know from previous discussion that the secondary structure varies for different proteins & it is likely that there is significant secondary structure in these chains, the comparison is probably fortuitous.

3) a)



F=0 The Application of force leads to the formation of a 2° structure called a "Blob" b)

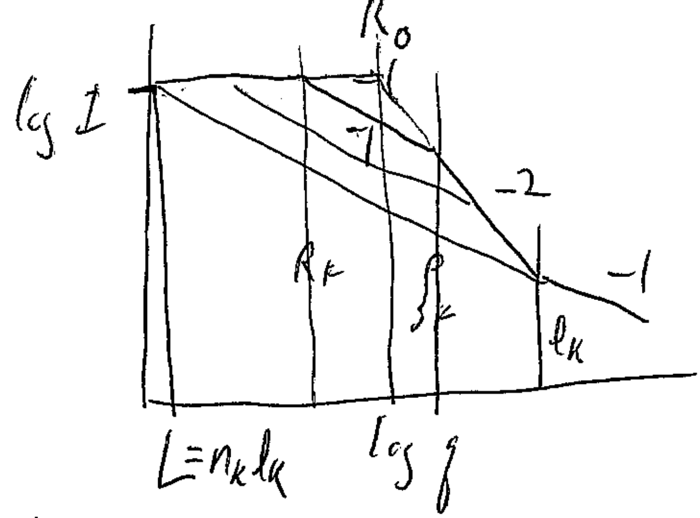


For a given force F there is a size ξ_F where $nl^2 \sim R^2 = \xi_F^2$ such that

$$F = \frac{3kTR}{nl^2} = \frac{3kT}{\xi_F} \quad \& \quad \boxed{\xi_F = \frac{3kT}{F}}$$

simple coil spring eqn.

c)



d) $F = \frac{3kT}{\xi_F} = \frac{3kTR}{nl^2}$ $F \sim T$ for ideal chain

e) $p = \frac{nkT}{V}$ Both depend linearly on T because both represent random Gaussian states, one for Kuhn units & one for gas atoms.