Polymer Properties Quiz 2
January 29, 2016

1) A random walk with no self-avoidance displays a mass fractal dimension of 2. In class it was mentioned that a star polymer will also display a mass fractal dimension of 2 if there is no self-avoidance (this is true of any thermally equilibrated polymer with no self-avoidance).

a) Demonstrate that the mass fractal dimension of a random walk is 2 by calculating, $\langle R^2 \rangle$ as the double sum of dot products of all bond vectors $\mathbf{r}_i$ and $\mathbf{r}_j$.
b) One way you could imagine a symmetric star polymer is to have two or more of the same random walks as in part "a" superimposed in the same space R^3. Use this approach to show that the mass fractal dimension is still 2 for a four arm star polymer.
c) How does the connectivity dimension c change for a four arm star polymer with z = 200? Consider that the total mass, z, is given by $z = p^c$, where p is the minimum path. For a symmetric star polymer, p is 2(z/f), where f is the number of arms.
d) What is the value of d_{min} for this symmetric four arm star polymer?
e) What happens to the polymer structure in going from a linear chain to a four-arm star?
f) What happens to the monomer density in the coil ($\rho = 1/c^*$) in going from a linear chain to a four arm symmetric star polymer?

2) The energy of a polymer chain with respect to chain deformations is obtained by a comparison between the probability function P(R) for the end-to-end distance R, and the Boltzmann function for a thermally equilibrated structure.

a) Obtain an expression for the energy of an isolated Gaussian polymer coil.
b) Use this energy to obtain an expression for the spring constant that governs the mechanical behavior of an isolated polymer chain.
c) How will increasing the molecular weight between crosslinks in a rubber impact the modulus?
d) In very cold environments it is found that tires can retain the flat spot due to being parked overnight making the car ride rough. This disappears after driving for a few minutes. Compare this observation to the energy expression that you have found in part "a".
e) Would the energy expression from part "a" be appropriate for a four arm star polymer?

ANSWERS: Polymer Properties Quiz 2
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1)

a) *Demonstrate that the mass fractal dimension of a random walk is 2 by calculating, $<R^2>$ as the double sum of dot products of all bond vectors* $\mathbf{r}_i$ *and* $\mathbf{r}_j$.

The chain is composed of a series of steps with no orientational relationship to each other.
So <R> = 0
$<R^2>$ has a value:

$$\left\langle R^2 \right\rangle = \sum_i \sum_j r_i \bullet r_j = \sum_i r_i \bullet r_i + \sum_i \sum_{j \neq i} r_i \bullet r_j$$

We assume no long range interactions so that the second term can be 0.

$$\left\langle R^2 \right\rangle = Nr^2$$

$$<R^2>^{1/2} \sim N^{1/2}\, l_K$$

b) *One way you could imagine a symmetric star polymer is to have two or more of the same random walks as in part "a" superimposed in the same space R^3. Use this approach to show that the mass fractal dimension is still 2 for a four arm star polymer.*

R is the same as above, z = 2N, so we have $<R^2> = 2N\, l_k$, the mass fractal dimension is still 2.

c) *How does the connectivity dimension c change for a four arm star polymer with z = 200? Consider that the total mass, z, is given by $z = p^c$, where p is the minimum path. For a symmetric star polymer, p is 2(z/f), where f is the number of arms.*

(ln z)/ (ln p) = c so c = (ln z)/ ((ln z) + ln(2/f)). For z = 200 and f = 4, c = 1.15. c should be larger than 1 since we have made the structure non-linear.

d) *What is the value of d_{min} for this symmetric four arm star polymer?*

$d_{min} = d_f/c = 2/1.15 = 1.74$.

e) *What happens to the polymer structure in going from a linear chain to a four-arm star?*

The star arms straighten out to maintain the mass fractal dimension at 2.

f) *What happens to the monomer density in the coil ($\rho = 1/c^*$) in going from a linear chain to a four arm symmetric star polymer?*

Linear chain: $\rho = z/R^3 = z^{1-3/df}$.

4-arm star: $\rho = 2z/R^3 = 2z^{1-3/df}$. The density doubles in this case or generally it increases by f/2.

2)

a) *Obtain an expression for the energy of an isolated Gaussian polymer coil.*

Boltzman Probability
For a Thermally Equilibrated System

$$P_B(R) = \exp\left(-\frac{E(R)}{kT}\right)$$

Gaussian Probability
For a Chain of End to End Distance R

$$P(R) = \left(\frac{3}{2\pi\sigma^2}\right)^{3/2} \exp\left(-\frac{3(R)^2}{2(\sigma)^2}\right)$$

By Comparison The Energy to stretch a Thermally Equilibrated Chain Can be Written

$$E = kT\frac{3R^2}{2nl_K^2}$$

b) *Use this energy to obtain an expression for the spring constant that governs the mechanical behavior of an isolated polymer chain.*

$$F = \frac{dE}{dR} = \frac{3kT}{nl_K^2}R = k_{spr}R$$

Assumptions:
-Gaussian Chain
-Thermally Equilibrated
-Small Perturbation of Structure (so it is still Gaussian after the deformation)

c) *How will increasing the molecular weight between crosslinks in a rubber impact the modulus?*

Increasing n drops the modulus so the rubber becomes weaker with higher molecular weight.

d) *In very cold environments it is found that tires can retain the flat spot due to being parked overnight making the car ride rough. This disappears after driving for a few minutes. Compare this observation to the energy expression that you have found in part "a".*

For the energy expression, increasing T increases the modulus making the rubber stiffer. In this observed phenomena, low temperature leads to a lower compliance that contradicts the energy expression. This is because lower temperatures reduce the contractile force of the polymer chains on the chain ends, but they also dramatically increase the relaxation time making the tire respond more slowly to deformation. The equilibrium modulus should be lower but the dynamic response time is much larger.

e) *Would the energy expression from part "a" be appropriate for a four arm star polymer?*

The energy expression relies on a mass fractal dimension of 2, it does not refer to the minimum dimension, so in that sense it should apply. The chain structure has changed in going to a branched chain, so you might expect that the mechanical response would be different and would not follow the predicted modulus. There are at least two ways to look at this.