020409 Quiz 3 Properties

1) The Flory-Krigbaum free energy for a chain is given by,

$$\frac{F_{FK}}{kT} \sim -\frac{3}{2}\left(\frac{R}{R_0}\right)^2 - \frac{1}{2}\left(\frac{R_0}{R}\right)^3\left(\frac{V}{b^3}\right)\left(\frac{R_0}{b}\right) = \frac{3R^2}{2Nb^2} - \frac{N^2V}{2R^3}$$

Show that this expression for the free energy gives the same result for the chain mass-fractal dimension as the Flory-Krigbaum approach using the probability of a chain of length N having and end-to-end distance R.

-You will need to **write** the Flory Krigbaum result (fifth power minus third power expression) and **obtain** $R^* \sim N^{3/5}$ from this FK expression as well as

-**obtaining** $R^* \sim N^{3/5}$ from the free energy expression shown above.

(Two calculations are needed. Make sure the units work out in your calculations.)

2) -**Write** an expression for the Flory radius, R_F, for a chain with χ between 0 and 1/2 in terms of N (number of Kuhn units), ξ_T (thermic blob size) and l_K (Kuhn step length).

-**Equate** this to your Flory-Krigbaum scaling relationship for RF in terms of χ, l_K and N to obtain an expression for ξ_T in terms of l_K, χ and N.

-**Explain** the dependence of ξ_T on N that you obtained.

-**What** three regimes are expected from this equation?

3) The intrinsic viscosity [η] is proportional to 1/ρ, where ρ is the density of the polymer coil, N_{coil}/V_{coil}.

-**Show** that for a theta solvent [η] scales with $N^{1/2}$.

-**What** is the scaling for and expanded coil?

-**What** is the scaling if the chain displays thermic blobs?

-**Explain** the values of "a" in the Mark-Houwink equation, $[\eta] = K N^a$, where "a" ranges from 0.5 to close to 1.

Answers: 020409 Quiz 3 Properties

1) a) From $\left(\frac{R^*}{R_0}\right)^5 - \left(\frac{R^*}{R_0}\right)^3 = \frac{9\sqrt{6}}{16}\frac{V}{b^3}\sqrt{N}$ and taking the high R* limit, the 3'rd power can be dropped. Using $R_0 = b\sqrt{N}$, we have

$$(R^*)^5 = \frac{9\sqrt{6}}{16}\frac{V}{b^4}R_0^6 \quad \textbf{so } R^* \sim \left(\frac{9\sqrt{6}}{16}Vb^2\right)^{\frac{1}{5}} N^{\frac{3}{5}} = b\left(\frac{9\sqrt{6}}{16}\right)^{\frac{1}{5}}(1-2\chi)^{\frac{1}{5}}N^{\frac{3}{5}}$$

b) From F_{FK}, the minimum in the free energy is obtained at R* given by,

$$\frac{dF}{dR} = 0 = -\frac{R^*}{R_0^2} + K\frac{R_0^3}{2R^{*4}}$$

where K = $\frac{V}{b^3}\left(\frac{R_0}{b}\right)$. Solving for R*,

$$R^{*5} = R_0^5\frac{K}{2} = R_0^6\frac{V}{b^4} = N^3Vb^2$$

so,

$$R^* \sim N^{\frac{3}{5}}V^{\frac{1}{5}}b^{\frac{2}{5}} = bN^{\frac{3}{5}}(1-2\chi)^{\frac{1}{5}}$$

2) $R_F = N^{3/5}\xi_T^{-1/5}l_K^{6/5}$

FK: $R^* \sim N^{\frac{3}{5}}V^{\frac{1}{5}}b^{\frac{2}{5}} = bN^{\frac{3}{5}}(1-2\chi)^{\frac{1}{5}}$

Equating the two we have: $\xi_T \sim l_K/(1-2\chi)$

The thermal blob size does not depend on N since it occurs at size scales less than R_F. When the thermal blob size is less than or equal to the Kuhn length then the chain is fully expanded. When the blob size is equal to R_F the chain is fully Gaussian and this occurs uniquely when $\chi = 1/2$. An intermediate condition where two scaling regimes are observed is seen when χ is between 0 and 1/2.

3) $[\eta] = K/\rho = KR_F^3/N = K\,N^{3/2}/N = K\,N^{1/2}$.

For a good solvent coil, $R_F = C\,N^{3/5}$ so, $[\eta] = K\,N^{0.8}$

The MH equation doesn't explain blob behavior so can not completely explain the scaling behavior of real polymer coils. Numbers larger than 0.8 for a are generally associated with rod like behavior.

For the thermic blob $R_F = N^{3/5}\xi_T^{-1/5}l_K^{6/5} = N^{3/5}l_K/(1-2\chi)$ so

$[\eta] = KR_F^3/N = K\,N^{3/2}/N = K\,N^{0.8}l_K^3/(1-2\chi)^3$, i.e. the thermic blob doesn't explain MH coefficients that vary from 0.8.