Quiz 4 Polymer Properties 070425

This week we discussed the spatial correlation function and the radius of gyration, R_g, The radius of gyration has some advantages over other measures of size for polymer coils in dilute solution, particularly those based on dynamic properties such as viscosity and diffusion. In class we considered that the radius of gyration can be calculate from: $\left\langle R_g^2 \right\rangle = \frac{1}{N}\sum_{i=1}^{N}\left(R_i - R_G\right)^2$ for a discrete structure (a structure that can be indexed from 1 to N such as a polymer chain with N units). For a continuous structure (such as a solid sphere) we can transform the summation to a normalized integral in 3-d space:

$$\left\langle R_g^2 \right\rangle = \frac{\int\limits_{r=0}^{R_{\max}}\int\limits_{\theta=0}^{2\pi} d\theta \int\limits_{\psi=0}^{\pi} d\psi \rho(r,\theta,\psi) r^4 dr}{\int\limits_{r=0}^{R_{\max}}\int\limits_{\theta=0}^{2\pi} d\theta \int\limits_{\psi=0}^{\pi} d\psi \rho(r,\theta,\psi) r^2 dr} \quad \text{or} \quad \frac{\int\limits_{z=small}^{l\arg e} dz \int\limits_{x} dx \int\limits_{y} dy \left(x^2 + y^2 + z^2\right)\rho(x,y,z)}{\int\limits_{z=small}^{l\arg e} dz \int\limits_{x} dx \int\limits_{y} dy \rho(x,y,z)}$$

where x, y, z or r go from the center of mass.

Calculate the radius of gyration for a rod ($R_g^2 = L^2/12$) by:

1) Following what we did in class except using $R^2 = (nl_K)^2$ rather than $R^2 = nl_K^2$.

   You will need the following math identity:

   29.9. $$\sum_{u=1}^{n} u^p = \frac{n^{p+1}}{p+1} + \frac{n^p}{2} + \frac{B_1}{2!}pn^{p-1} - \frac{B_2}{4!}p(p-1)(p-2)n^{p-3} + \cdots,$$

   omitting terms in n^0 and those that follow.

   For values of B_1, B_2, $\cdots$, see **45.**

   The above results may be used to find the sum of a series whose nth term is made up of n, n^2, n^3, etc.

   H. B. Dwight "Tables of Integrals and other Mathematical Data" (1957)

2) Calculate the radius of gyration for a rod using the integral form above and assuming that the rod is infinitely thin. This means that the integrals in y and x are 1 in the second integral equation. The density function for a rod has a value of ρ for z between -L/2 and L/2 and for x=y=0.

3) In many problems in polymers it is useful to represent the polymer chain through matrix math. From our discussion of the radius of gyration explain what is the relationship between a polymer coil and a matrix.

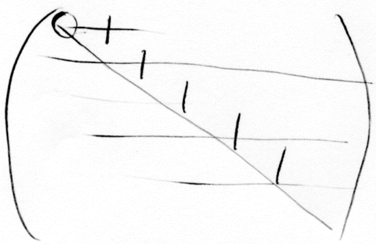
4) Fractals are characterized by a feature termed *self-similarity*, that is the structure is *size-scale invariant*. This means that if we look at a polymer coil at low magnification or at high-magnification the structure seems to be the same. For mathematical fractals this self-similarity is true from the smallest sizes to the largest but for real fractals it is true only over a limited range of size from the Kuhn length to the overall coil size. In the derivation of the radius of gyration for the polymer coil we invoked self-similarity. Explain how this was used to obtain the radius of gyration for a polymer coil

5) In class we discussed the *ghost particle* of Wilson which involves the translation and averaging of a particle to describe the correlation function and the scattered intensity due to binary interference. Explain the relationship of the *ghost particle* to scattering, the radius of gyration and Guinier's Law: $I(q, R_g) = G \exp(-q^2R_g^2/3)$ where G is a constant equal to Nn_e^2.

1) $\langle R_g^2 \rangle = \frac{1}{2N^2} \sum_{i=1}^{N} \sum_{j=1}^{N} \underbrace{(r_i - r_j)}_{\Delta r}{}^2$

For a rod $(\Delta r)^2 = (j-i)^2 l_k^2$

$$= \frac{l_k^2}{N^2} \sum_{i=1}^{N} \sum_{j=i}^{N} (j-i)^2$$



$z = n-1$

$(1)\, z + 4(z-1) + 9(z-2) + \cdots 1 z^2$

$$\sum_{p=1}^{z} (z+1-p)(p)^2$$

$$= (z+1) \sum_{p=1}^{z} p^2 - \sum p^3$$

$$\sum_{p=1}^{z} p^2 = \frac{z^3}{3} + \cdots$$

$$\sum_{p=1}^{z} p^3 = \frac{z^4}{4} + \cdots$$

$$\sim \frac{z^4}{3} - \frac{z^4}{4} = \frac{4}{12} z^4 - \frac{3}{12} z^4$$

$$= \frac{z^4}{12}$$

(2)

$$\langle R_j^2 \rangle = \frac{l_k^2}{N^2}\frac{z^4}{12} \sim \frac{z^2 l_k^2}{12} = \frac{L^2}{12}$$

$z = N-1$

2)

$$\langle R_j^2 \rangle = \frac{\int_{-L/2}^{L/2} \cancel{z}^2 \, dz}{\int_{-L/2}^{L/2} dz} = \frac{\left[\frac{z^3}{3}\right]_{-L/2}^{L/2}}{2\left(\frac{L}{2}\right)}$$

$$\langle R_j^2 \rangle = \frac{\frac{1}{3}\left(\frac{L^3}{8} + \frac{L^3}{8}\right)}{L} = \frac{1}{3}\left(\frac{L^2}{4}\right) = \frac{L^2}{12}$$

3) We found the summation

$$\frac{l_k^2}{2N^2}\sum_{i=1}^{N}\sum_{j=1}^{N} |(i-j)|$$

could be understood using the matrix of values

$$\begin{array}{c|cccccccc}
 & 1 & 2 & 3 & 4 & 5 & \cdots & n \\
\hline
1 & 0 & 1 & 2 & 3 & 4 & 5 & \\
2 & 1 & 0 & 1 & 2 & 3 & 4 & \\
3 & 2 & 1 & 0 & 1 & 2 & 3 & \\
4 & 3 & 2 & 1 & 0 & 1 & 2 & \\
5 & 4 & 3 & 2 & 1 & 0 & 1 & \\
\vdots & & & & & & & \\
n & & & & & & & 0
\end{array}$$

i, j

etc.

Basically binary interactions lead to a matrix of values + for spatial interactions Flory uses this for calculations of the free energy due to bond rotation for instance in the second book.

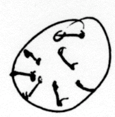
4) When we assume that

$$(r_i - r_j)^2 \Rightarrow l_K^2 |j-i|$$

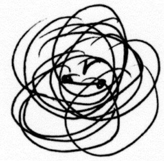
we assume that small parts of the coil have the same scaling $R^2 \sim n l_K^2$ as the whole coil.

5) 2 points separated by "r" are tossed into the sample. The probability for scattering equals the probability the two ends are in a "phase"

We consider all orientations that meet this condition



or keep ⟶ fixed & average particle



→ Wilson Ghost Particle (1949)

This is a probability function (Gaussian)

$$\gamma(r) = \exp\left(-\frac{3r^2}{4R_g^2}\right)$$

where R_g^2 is proportional to the variance.

The RMS size of this Ghost Particle is proportional to $\langle R_g^2\rangle^{1/2}$

The scattered intensity is the Fourier Transform of this correlation function

$$I(q) = G\exp\left(-\frac{q^2R_g^2}{3}\right)$$

which is Guinier's Law