Quiz 9 Polymer Properties October 24, 2014

a) The scattering Function for a sphere is given by:

$$I(q) = 9G\left[\frac{\sin qR - qR\cos qR}{(qR)^3}\right]^2 \quad (1)$$

(for example see Pedersen, J. S. (1997). *Adv. Colloid Interface Sci.* **70**, 171-210 or RJ Roe's text).
where R is the radius of the sphere, G is proportional to the square of the volume of the sphere times the density squared. Show that equation (1) agrees with Guinier's Law at low-q, and with Porod's Law at high-q ($I(q) \sim Sq^{-4}$ where S is the sphere surface area).

$$\sin x = x - \frac{1}{6}x^3 + \frac{1}{120}x^5 - \frac{1}{5040}x^7 + \ldots \text{ for } -\infty < x < \infty$$

$$\cos x = 1 - \frac{1}{2}x^2 + \frac{1}{24}x^4 - \frac{1}{720}x^6 - \ldots \text{ for } -\infty < x < \infty$$

$\langle\cos^2\theta\rangle = \langle\sin^2\theta\rangle = ½$, and $\langle\sin\theta\cos\theta\rangle = 0$

b) Show that the radius of gyration for equation (1) agrees with the radius of gyration for a sphere. (Calculate the radius of gyration for a sphere in terms of R then compare with what you obtain by equating the low-q extrapolation of (1) with Guinier's Law and solving for R_g.)

c) The Debye-Bueche function is often used to describe scattering from solid objects of unknown structure.

$$p(r) = K\exp\left(-\frac{r}{\xi}\right) \qquad \textbf{Debye-Bueche Function} \qquad I(q) = \frac{G}{1+q^4\xi^4} \quad (2)$$

Critique equation (2) by comparison with Gunier's Law.
Does equation (2) follow Porod's law at high-q? (Is the prefactor proportional to S?)

d) Debye derived equation (3) for polymers in dilute solutions,

$$g(q)_{Gaussian} = \frac{2}{Q^2}\left[Q - 1 + \exp(-Q)\right]$$

where $Q = q^2Nb^2/6 = q^2R_g^2$ (3)

Can this equation be used for polymers in dilute solution? Explain why by extrapolation to high-q.
Can equation (3) be used for polymer chains in a melt?

e) The radius of gyration for a polymer is equal to the end-to-end distance divided by √6 for a Gaussian chain. How is the hydrodynamic radius related to the end-to-end distance? (You may need to give a structural picture of the hydrodynamic radius to answer this.)

ANSWERS: **Quiz 9 Polymer Properties October 24, 2014**

1) a) Substituting the power series for sin and cos we obtain:

$y = qR$

$$9G\left[\frac{\cancel{x} - \frac{x^3}{3!} + \frac{x^5}{5!} - \left[\cancel{x} - \frac{x^3}{2!} + \frac{x^5}{4!} - \frac{x^7}{6!}\right]}{x^3}\right]^2$$

$$= 9G\left[\frac{\frac{x^3}{3} - \frac{1x^5}{30}}{x^3}\right]^2 = 9G\left[\frac{1}{3} - \frac{1x^2}{30}\right]^2$$

$$= G\left[1 - \frac{x^2}{10}\right]^2 \cong G\left[\exp\left(\frac{-q^2R^2}{10}\right)\right]^2$$

$$= G \exp \frac{-q^2R^2}{5}$$

Compare with Guinier's law

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

So $\frac{R_g^2}{3} = \frac{R^2}{5}$ or $\boxed{R_g^2 = \frac{3}{5}R^2}$

At high-q you expand the squared term and find the average values for the trig terms at high-q: $\langle\cos^2\theta\rangle = ½$; $\langle\sin^2\theta\rangle = ½$; $\langle\cos\theta \sin\theta\rangle = 0$. So the function yields $9G/(2R^4q^4)$. G is proportional to V^2 or R^6, so we have $S \sim R^2$.

b) For a sphere we take the integral of R4 divided by the integral of R2 to obtain $R_g^2 = 5/3\ R^2$. The low-q extrapolation of equation (1) yields the same answer.

c) Equation (2) is the first two terms of G $\exp(-q^4\xi^4)$ which is not the same form as Guinier's Law so the function can not be correct.
At high-q, using $G \sim V^2$, yields R^6/ξ^4 which has the units of area, but the correlation length is not directly related to the surface to volume ratio so the expression is muttled.

d) Equation (3) can only be used for Gaussian polymers so it can not be used for polymers in dilute solution which display good solvent scaling. I can be used for polymers in the melt.

e) There is not good direct relationship between the hydrodynamic radius and the end-to-end distance of a polymer chain. It depends on the degree of drainage of the coil for one thing.