Quiz 7 Polymer Properties
March 4, 2016

Debye obtained the following scattering function for a single Gaussian polymer coil,

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

$$\text{where } Q = q^2Nb^2/6 = q^2R_g^{\ 2} \qquad (1)$$

The function was derived following the same logic that we used to obtain the radius of gyration for a Gaussian polymer chain.

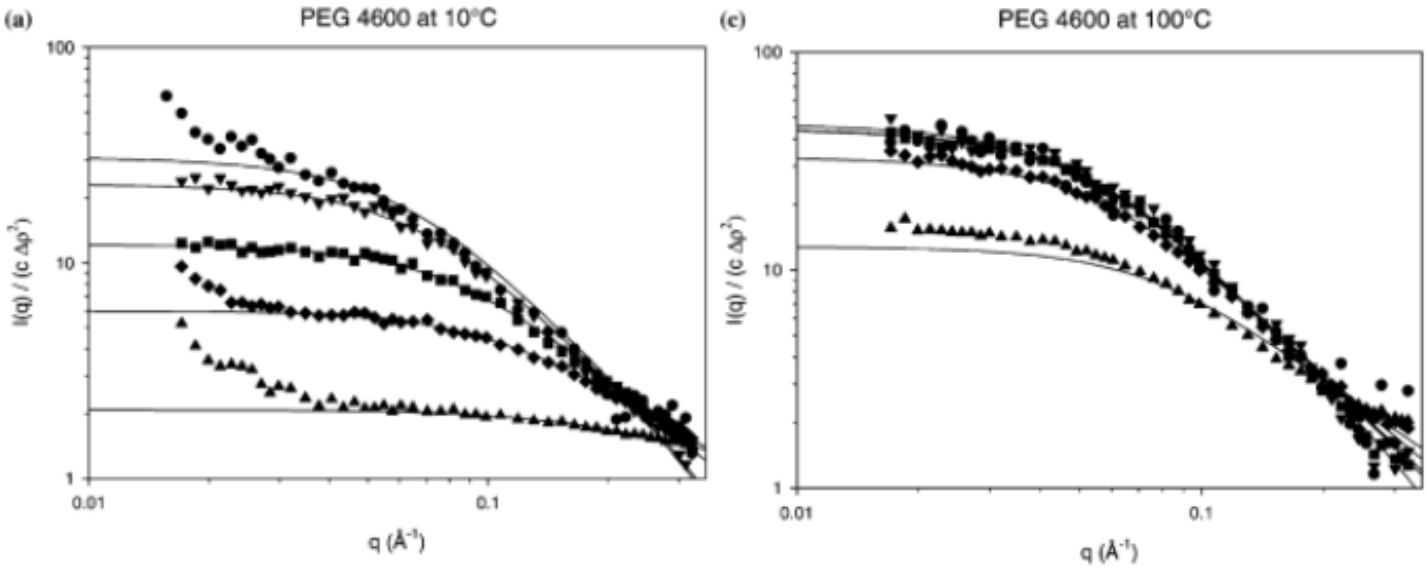
a) How is the radius of gyration for a Gaussian chain related to the chain end to end distance $n^{1/2}l$?

b) Show that Debye's function matches Guinier's law at low-q.

c) Explain why you would expect a power-law of -2 for a fractal structure with $d_f = 2$ using $I(q) = N\, n_e^2$.

d) Show that Debye's function displays this behavior at high-q.

e) Explain the behavior seen in the following two plots of Pederson and Sommer that show increasing concentration from 1, 2, 5, 10, and 20% polyethylene glycol in water at two temperatures.



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ANSWERS:

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a) $R_g = n^{1/2}\, l/\sqrt{6}$

b) At low q, Q is small so the exponential term can be expanded to $1-Q+Q^2/2-Q^3/6+\ldots$ The bracketed term becomes $Q^2/2-Q^3/6$. Dividing by Q^2 from the lead term, and using the exponential expansion for low-Q we have $\exp(-q^2R_g{}^2/3)$.

c) For a fractal structure at sizes between the overall size, R and the substructural size d_p, the structure can be thought of as composed of spheres of radius $r = 2\pi/q$. Each sphere has $n = (r/d_p)^{df}$ primary structures and there are $M=N/n = (R/r)^{df}$ spheres in the fractal. The scattering at a given value of q or r is given by $I(q) = Mn^2 = (R/r)^{df}\,(r/d_p)^{2\,df} = (R^{\,df} / d_p{}^{2\,df})\, r^{\,df} \sim q^{-df}$

d) At high-q, Q is large so the exponential goes to 0 and Q>>1 so the bracketed term is Q. The scattering is then $I(q) = 2/Q = 2/q^2R_g{}^2 \sim q^{-2}$ or $d_f = 2$.

e) As the concentration increases structural screening occurs that obscures the low-q scattering at sizes larger than the correlation length. The screening is related to the interaction parameter/ second virial coefficient, that have a temperature dependence.