Quiz 9 Polymer Properties
March 12, 2020

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.

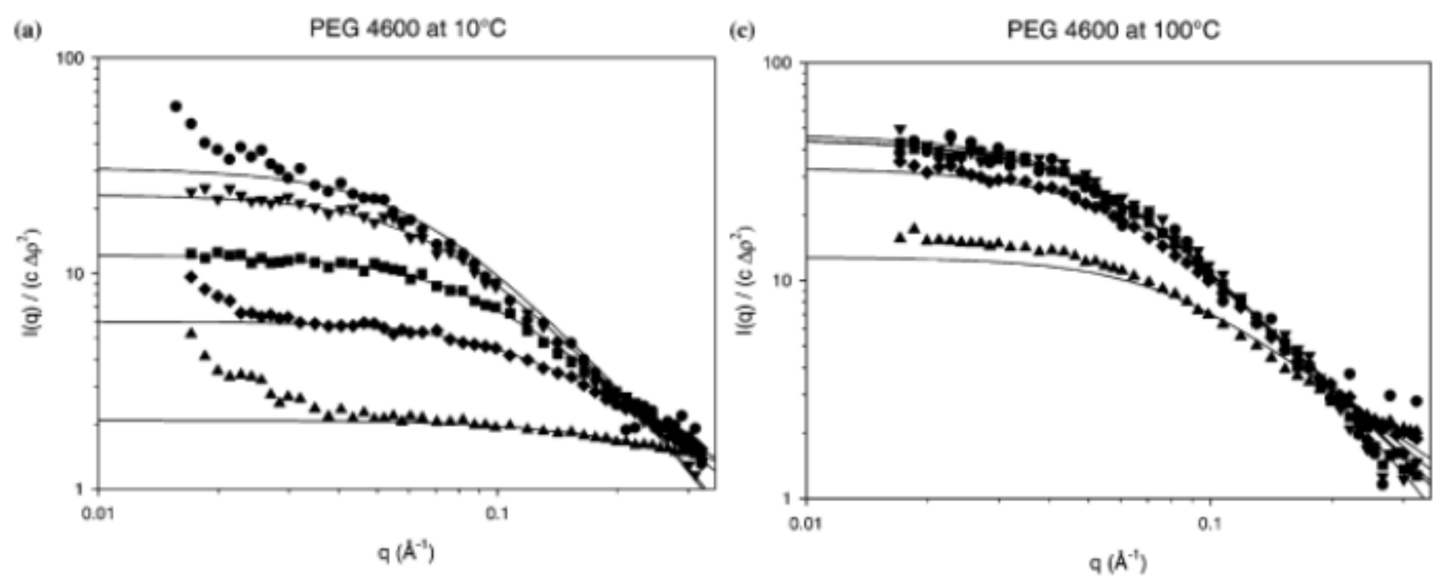
a) Show that Debye's function matches Guinier's law at low-q.

b) Explain why you would expect a power-law of -2 for a fractal structure with $d_f = 2$ using $I(q) = N\,n_e^2$. Consider that you can decompose the Gaussian chain into sub-chains of size $r = 2\pi/q$ that are also Gaussian and which fit into a sphere of size r. There are $N(r)$ spheres in a chain, and $n_e(r)$ monomers of length l in a sphere. Use Gaussian scaling for both the sub-chains and for the overall chain then solve for Nn_e^2 as a function of r, then convert to q using $r \sim 1/q$.

c) Show that Debye's function displays this behavior ($I(q) \sim q^{-2}$) at high-q.

d) 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 (top to bottom) in water at two temperatures. Notice that the scattered intensity is normalized by the concentration and it is a log-log plot with a power-law of -2 at high-q. Notice that the rate of change of the concentration reduced intensity with concentration is larger for a lower temperature. Is this an LSCT or a UCST system? What happens to the scattering curves at the critical temperature (phase separation temperature)?

e) A randomly arranged polydisperse disk also displays Guinier's law, $I(q) = G_{disk}\exp(-q^2R_{g,disk}^2/3)$, at low-q and a power-law decay of -2 at high q, $I(q) = B_{disk}q^{-2}$. How could the scattering from a disk be distinguished from the scattering for a polymer coil?



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ANSWERS:
Quiz 7 Polymer Properties
March 4, 2016

a) 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 $\exp(-q^2R_g^2/3)$.

b) 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 $I(q) = Mn^2 = (R/r)^{df} (r/d_p)^{2\ df} = (R^{df} / d_p^{2\ df})\ r^{df} \sim q^{-df}$

c) 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 $d_f = 2$.

d) 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 or second virial coefficient, that have a temperature dependence. The second virial coefficient goes to 0 at the critical point so the curves would not depend on concentration, all fluctuations are equally probable.

e) The B/G ratio is different for a disk.