Quiz 7 Polymer Properties
March 4, 2016

1) This week we discussed the physics of a scattering event.

a) A diamond is placed in a monochromatic, collimated x-ray beam. The diamond is close to a perfect crystal. Explain why no diffraction is observed based on the discussion in class.

b) How would you modify the measurement in part "a" to observe diffraction from a diamond?

c) Spinodal decomposition occurs when a phase spontaneously grows from random concentration fluctuations. The process is governed by a balance between the rate of diffusion, the rate of phase separation, and the enthalpy change driving the phase separation event. For polymers these issues collude to create phases at 0.1 to 5 micron in separation distance that grow on a minute time scale, making light scattering from the process possible. The spinodal structure looks like a random 3d web in a micrograph. Light scattering results in a single diffraction peak. Why do you think this random web structure generates a diffraction peak in light scattering? (Think about what is necessary for a diffraction event.)

d) In contrast to spinodal decomposition, growth of a phase by nucleation and growth does not result in a diffraction peak in scattering. Domains are roughly spherical and form at nucleation seeds by normal diffusion from high concentration to low concentration at the depleted growth front. Domains are on the order of several microns in size and have smooth sharp interfaces with a discrete surface. Describe the scattering you might expect in this case.

e) Nonwoven fabrics are formed by randomly spinning a fiber from spinnerets to form a "web" which is a relatively dilute structure of random walk fibers. If a fiber coil had an overall size of 5 micron describe the light scattering you would expect from such a non-woven material.

2) 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) Real fractals display two size limits. One is the overall size, R_g. What is the other limit for a polymer chain? Can Debye's function describe scattering in the q regime where this limit is reached? How or Why?

__ANSWERS:__
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1) a) In order to observe a diffraction event the Bragg condition must be met and the crystal plane that is causing the diffraction must be aligned so that the q vector is normal to the diffracting plane. For a randomly placed crystal it is highly unlikely that the plane will be properly oriented for a diffraction event to occur.

b) The diamond could be rotated and this possibly could result in a diffraction event (Rotating crystal method). The diamond could be ground to a powder this would result in a diffraction event (Powder pattern). A polychromatic beam could be used rather than a monochromatic beam (Laue method).

c) The arms of the "random" web are regularly spaced since they result from a balance of transport kinetics, growth kinetics, and thermodynamic driving force. This regular spacing is all that is needed for a single diffraction peak. For higher order peaks it is necessary to have long range repeat in a lattice.

d) This is expected to generate a scattering curve displaying Guinier's Law at low-q and Porod scattering, q^{-4} at high-q.

e) This would generate a scattering pattern similar to that for a self-avoiding walk, Guinier's law at low-q and a power-law decay of -5/3 slope at high-q.

2) 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) The small-scale limit is the Kuhn length that should display a power-law of -1 slope in a log-log plot. The Debye function only displays a power-law decay of -2 at high-q so it cannot describe the Kuhn length.