120508 Quiz 4 Polymer Properties

1) The time auto-correlation function, $g^1(q,\tau)$ is used to obtain the diffusion coefficient from a noise pattern created by the change in scattered intensity with time from a colloidal suspension.

   a) Sketch a plot the intensity as a function of time for large particles, medium sized particles and small colloidal particles. Are these curves different? Why?

   b) What is the time correlation function $g^2(q,\tau)$, show how it is determined from an intensity versus time plot.

   c) What is the value of $g^2(q,\tau)$ when $\tau = 0$ and when $\tau = \infty$?

   d) Write an expression for $g^1(q,\tau)$ as a function of $g^2(q,\tau)$ using your answer to "c" to define the parameters.

   e) How can the hydrodynamic radius be obtained from $g^1(q,\tau)$?

2) The following scattering function has been proposed by Benoit [H. Benoit, *J. Polym. Sci.*, **1953**, XI, 507] for scattering from Gaussian star polymers (f is the number of arms, b is the segment length, n is the number of segments per arm). (Star polymers are polymers with arms emanating from a center point.)

$$S_{Star}\left(q,b,n,f\right) = \frac{P_{11}}{f} + \frac{f-1}{f}P_{12}$$

$$P_{11}\left(q,b,n,f\right) = \frac{2}{\left(xn\right)^2}\left(e^{-xn} - 1 + xn\right)$$

$$P_{12}\left(q,b,n,f\right) = \frac{\left(1-e^{-xn}\right)^2}{\left(xn\right)^2}$$

$$x = \frac{\left(qb\right)^2}{6}$$

   a) Show that the first term (P_{11}) displays Gaussian scaling at high-q.

   b) Obtain the radius of gyration for the first term by extrapolating the first term to low-q and comparing with Guinier's law.

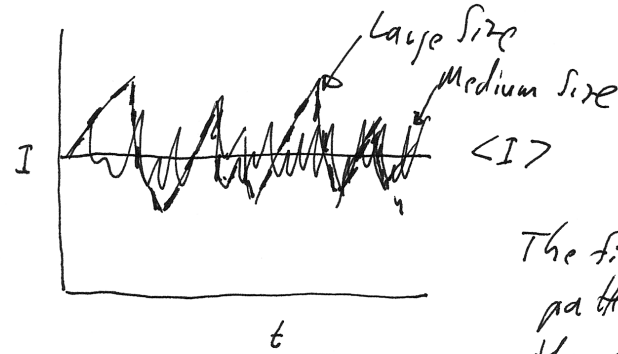
   c) Explain what part of the star structure you think the first term describes.

   d) Show that the second term is non-fractal in nature (fractal structures display a power-law decay between -1 and -3).

   e) Do you think that this function could describe a star polymer with Gaussian arms? Explain your answer.

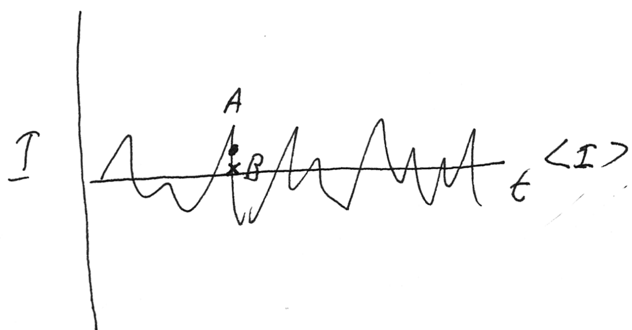
Answers: 120508 Quiz 4 Polymer Properties

1) a)



The finer the noise pattern the smaller the particles

b)



$$g^2(q,\tau) = \frac{\langle I(t)\, I(t+\tau)\rangle}{\langle I(t)\rangle^2}$$

Compare two intensities separated by τ
Multiply these two intensities and
take an average over all starting times, t_0.
This average at τ is normalized by
the value at $t=\infty$; $\langle I(t)\rangle^2$.

c) at $\tau = \infty$ $g^2(q,\tau) = 1$ & at $\tau = 0$ $\langle I(t) I(t+\tau)\rangle = \langle I^2(t)\rangle$

so $g^2(q,\tau) = \frac{\langle I^2(t)\rangle}{\langle I(t)\rangle^2}$

d) $$g^2(q,\tau) = 1 + \beta\left(g^1(q,\tau)\right)^2$$

$$\beta = \left(\frac{\langle I^2(t)\rangle}{\langle I(t)\rangle^2} - 1\right)$$

e) $$g^1(q,\tau) = \exp\left(-q^2 D \tau\right)$$

$$D = \frac{kT}{6\pi\eta R_H}$$

2) a) at high q $\quad e^{-xn} \Rightarrow 0$

& $xn - 1 \Rightarrow xn$

$$P_{11}(q\to\infty) \sim \frac{2}{xn} = \frac{2(6)}{q^2 n b^2}$$

$d_f = 2 \equiv$ Gaussian

b) at low q $\quad e^{-xn} \Rightarrow 1 - xn + \frac{(xn)^2}{2} - \frac{(xn)^3}{6} + \cdots$

$$P_{11}(q\to 0) \sim 2\left(\frac{1}{2} - \frac{xn}{6} + \cdots\right) \sim \exp\left(\frac{-xn}{3}\right)$$

Guinier's Law $\exp\left(-\frac{q^2 R_g^2}{3}\right) \therefore R_g^2 = \frac{nb^2}{6}$

c) The first term describes scattering from the arms as independent contributions to the overall scattering pattern.

d) at high-q $e^{-xn} \to 0$

$$P_{12} \Rightarrow \frac{1}{(xn)^2} = \frac{36}{q^4 b^4 n^2}$$

$P_{12} \sim q^{-4}$ so this is a non-fractal scattering law

e) There should be no part of the star scattering that would display a q^{-4} scaling so this function is erroneous.