120201 Quiz 3 Morphology of Complex Materials

1) Several measures of size are available for a protein molecule. In class we discussed R_g, R_h and the actual size R. R_h could be determined by a viscosity measurement or by dynamic light scattering (DLS).

a, b, c) Consider tobacco mosaic virus TMV (a rod structure of 2130 globular coating proteins with 158 residues each surrounding a single RNA strand of 6400 bases), lysozyme (129 residue globular protein found in egg whites), and thylakoid soluble phosphoprotein TSP9 (105 residue natively unfolded protein found in plants). For these three cases how would R_g, R_h and R differ? (Sketch the structure and show roughly what the three values are.)

d) Would the value of R_h be different if it were measured for TMV using dilute solution viscosity and by DLS? Explain your answer.

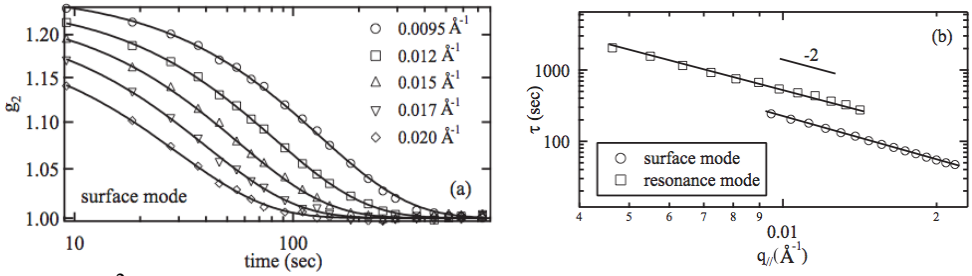
e) It has been noted that $R_h/R_g \sim 0.6$-0.7 for linear polymers in solution, 0.8-1.0 for highly branched polymers (hyperbranched) and 1.29 for hard spheres*. From your sketches in parts a, b, and c comment on these ratios.

* Akcasu, A. Z.; Han, C. C. *Macromolecules* **1979**, *12*, 276.
Muchtar, Z.; Schappacher, M.; Deffieux, A.; *Macromolecules* **2001**, *34*, 7595.
Kharchenko, S. B.; Kannan, R. M.; Cernohous, J. J.; Venkataramani, S. *Macromolecules* **2003**, *36*, 399.
Burchard, W.; Schmidt, M.; and Stockmayer, W. H. *Macromolecules* **1980**, *13*, 1265.

f) Which of the three structures in parts a, b, and c would display static scattering with a power law decay of slope -1 in a log intensity vs. log q plot? Why?

2) In PRL 104 066101 (2010) by T. Koga et al., dilute gold nanoparticles were embedded in a polystyrene thin film and the viscosity of the film in the melt was measured using x-ray photon correlation spectroscopy which is similar to dynamic light scattering except that it uses x-rays and was done in reflection from a surface.

a) Koga shows the following plot for variable incident angle in a reflection measurement (inset is q, higher q = higher angle = deeper penetration in the film).



What is g^2? (Sketch the intensity versus time for the top and bottom curves and explain roughly how the g_2 curves were obtained from these curves.)

b) The second plot shows relaxation time versus q. Why does this follow time ~ size^2 (q^{-2})? (That is, distance ~ time$^{1/2}$.)

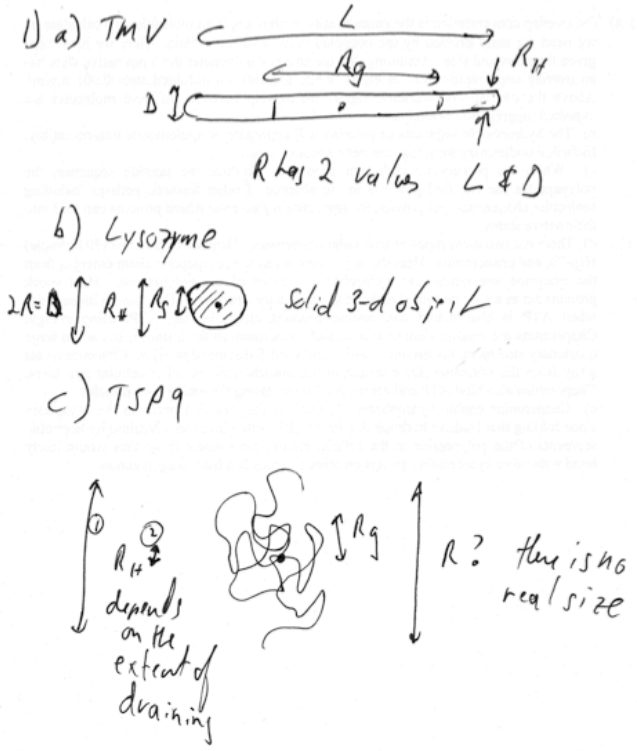
3) Guinier's law is the primary method to determine R_g.

a) Explain how Guinier's law is a Gaussian function. (Give the function and explain what the standard deviation is and why it is Gaussian.)

b) Why is Guinier's law a Gaussian function. (Show the Gaussian structure that is the basis for Guinier's law and describe its origin.)

ANSWERS 120201 Quiz 3 Morphology of Complex Materials

1) a), b), c)



d) The value from viscosity is based on an interpretation of the intrinsic viscosity for an equivalent sphere, the value from DLS involves an assumption that Stokes' law is followed for the viscosity and that the fluctuation dissipation theorem can be followed for the structure, that is that fluctuations on a molecular scale caused by thermal motion dissipate through the macroscopic mechanism of viscosity. The assumptions are different, DLS assumptions are a bit more hairy. There is no reason to believe that the values would be the same.

e) In a) it looks like TMV would have a much smaller R_h than R_g so R_h/R_g should be at a minimum though my sketch looks like a smaller value than 0.6.
In c) the ratio could be almost anything since it depends on the extent of draining for the coil. A ratio of 1 is possible.
In b) R_g should be smaller than R_h, this agrees with the value of 1.29 expected for the ratio of R_h/R_g for spheres.

f) The rod displays a power-law decay in intensity of q^{-1}. This is because it is the unique structure that is 1-dimensional. Power-law scattering follows $I(q) \sim q^{-df}$.

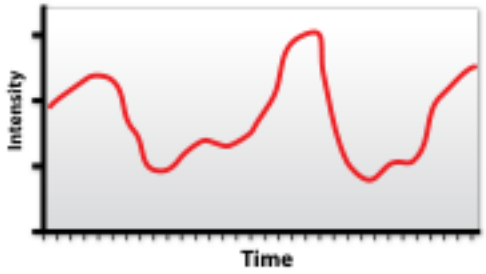
2) g^2 is the autocorrelation function,

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

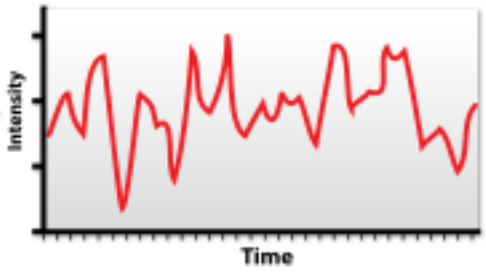
where I is the intensity measured at time t and a time t+τ. The intensity at t and t+τ are multiplied and averaged and normalized by the square of the mean intensity to arrive at g^2. g^2 is related to g^1 by,

$$g^2(q;\tau) = 1 + \beta\left[g^1(q;\tau)\right]^2$$

Top Curve:



Bottom Curve:



The intensity varies slowly in the top curve so the correlation in intensity remains high for a longer time. The correlation at τ = 0 is 1 since the intensity is the same, at longer τ the correlation drops since it is more likely that the intensity at t+ τ will be a random number leading to an average of 0 the longer τ is.

b) τ follows q^{-2} since it is a diffusion process where the distance a particle travels follows on average the square root of time. This is the case since the motion is random, that is, there is no correlation between position at time t and position at time t+ τ for a diffusing particle. Consider the average distance traveled is 0 since motion is random and it can move forward and backward equally, then the lowes order moment with a value is the mean square distance traveled $\langle R^2 \rangle$. This can be calculated from,

$$\left\langle R^2 \right\rangle = \int_{t=0}^{t}\int_{\tau=0}^{t} r_t \bullet r_{t+\tau}\, dt\, d\tau = \int_{t=0}^{t} r_t^2\, dt + \int_{t=0}^{t}\int_{\tau\neq 0}^{t} r_t \bullet r_{t+\tau}\, dt\, d\tau = tr^2$$

where r is a unit scalar of position. The third equality is true since the second term just before the final expression is 0 for a random process. So distance squared (mean square distance) goes linearly in time or distance goes with the square root of time for random (diffusive) motion.

3) a) The Guinier function is,

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

This is a Gaussin in q since it is a negative exponential of the square of the argument similar to,

$$P(x) = G\exp\left(\frac{-x^2}{2\sigma^2}\right)$$

The standard deviation for the Guinier function is then, $\sigma = \frac{\sqrt{3/2}}{R_g}$.

b) For any structure the scattered intensity is the Fourier transform of the pair wise autocorrelation function p(r). The transform of a Gaussian is a Gaussian so Guinier's law is related to a Gaussian correlation function. The correlation function is the probability that a vector, randomly placed in a structure will have the same structure found at a distance (r) from the original point placed in the structure. If we fix the initial point and rotate the particle and sum these orientations then sum all of the possible starting points we arrive at a cloud structure that is densest in the center and decays following a bell shaped curve or a Gaussian density profile. The transform of this Gaussian density profile is Guinier's law.