100227 Homework 6 Polymer Properties

- This week we considered the Debye scattering function for polymer chains, the Guinier function and power-law scattering. Use a computer to plot the Debye scattering function and Guinier's law on a log-log plot. Indicate over what range of scattering vector the Guinier function is appropriate for a polymer coil.
- 2) Analytically demonstrate what you have shown in question 1 by extrapolating the Debye function.
- 3) What mathematical behavior does the Debye function follow at high-q in your plot? Analytically demonstrate this using an extrapolation of the Debye function.
- 4) From your graph, measure the parameters associated with the high-q behavior of the Debye function by extrapolating the high-q curve to q = 1 and compare these parameter to the values you determined analytically in question 3.
- 5) The Ornstein-Zernike function, $\frac{1}{I(q)} \sim 1 + \frac{q^2 \xi^2}{2}$, is often proposed as a substitute for the Debye function

because it is easy to take derivatives and integrals of this function. Make a new log-log plot to compare this function with the Debye function for polymer coils.

- 6) Extrapolate this function to low-q and compare with Guinier's Law to obtain an expression for the radius of gyration.
- 7) The Debye function describes a single average polymer coil that does not display polydispersity in chain length. Consider how polydispersity effects scattering from a polymer coil by calculating the Debye function for a series of molecular weights (100) distributed with a log-normal distribution in radius of gyration (use a geometric mean of 100 Å and a geometric standard deviation of 1.6). Find the radius of gyration of the resulting polydisperse curve by fitting this calculated function with Guinier's law and plot the polydisperse and a monodisperse scattering function using this fit radius of gyration and the fit I(0) (or G) in the Debye function on the same log-log plot.
- 8) Describe the shift in the scattering curve associated with polydispersity and compare this shift with the shift observed in your plot of the Ornstein-Zernike function.
- 9) In polymer thermodynamics the free energy is calculated from the molecular weight of the polymer chain generally assuming that the chains are monodisperse. Scattering can be used to determine the enthalpy of mixing and the molecular weight. How would the result differ if the Ornstein-Zernike function were used rather than the Debye function?
- 10) The Ornstein-Zernike function is obtained by simply using the time correlation function from DLS, $exp(-t/\tau)$, as an ad-hoc spatial correlation function, $exp(-r/\xi)$ with no justification. This correlation function Fourier transforms to the O-Z function. List some of the main differences between time and space. Is time really the fourth dimension? Does it make sense to have a non-symmetrical, spatial correlation function?
- 11) From your calculation of a Gaussian chain structure in the first homework you have obtained a table of x, y, z for the chain unit positions. The correlation function, C(r), can be calculated as the average number of chain units separated by a distance "r". Make a matrix of all values of r_{ij}² for your simulated chain then bin this data into C(r) versus r bins with r steps of about 1 (for instance, a 10,000 unit chain r could vary from 0 to 1000 in steps of 1). Plot the log of your correlation function C(r) versus the log of r and comment on the plot.