

Che 210B

Homework 6

Due Thursday, February 24, 2005

1. Find R_g for an infinitely thin rod of length L .

2. Muralami, Norisuye, and Fujita measured the dimensions of a series of poly(hexyl isocyanate) specimens; PHIC is a reasonable representation of a worm-like chain. Given the following data, estimate the persistence length, ℓ_p , and the molecular weight per persistence length, M_p . The best way to do this is to prepare two log-log plots on the same scale, one of the data ($\langle R_g^2 \rangle$ vs. M), and another of the Kratky-Porod model in reduced units ($\langle R_g^2 \rangle / \ell_p^2$ vs. M/M_p). By obtaining the best superposition, ℓ_p and M_p can be determined. The Kratky-Porod expression linking L/ℓ_p and R_g is

$$R_g^2 = \langle s^2 \rangle \cong \left(\frac{L\ell_p}{3} - \ell_p^2 + \frac{2\ell_p^3}{L} + \frac{2\ell_p^4}{L^2} \left(e^{-\frac{L}{\ell_p}} - 1 \right) \right)$$

$M / 10^4 \text{ g/mol}$	$\langle s^2 \rangle / 10^{-10} \text{ cm}^2$	$M / 10^4 \text{ g/mol}$	$\langle s^2 \rangle / 10^{-10} \text{ cm}^2$
6.8	0.051	94.7	1.65
8.14	0.068	117	2.08
11.2	0.107	149	2.67
13.0	0.144	169	3.13
18.0	0.223	2.41	4.63
25.0	0.352	318	6.29
31.1	0.467	334	6.67
39.0	0.603	463	10.0
50.5	0.836	724	17.4
65.6	1.13		

3. Consider scattering from an incompressible, non-interacting, ternary mixture. Show that it is always possible to designate one component as the “solvent”, s, and the other two “a” and “b”, such that:

$$I(\mathbf{k}) = (a_a - a_s)^2 S_{aa} + (a_b - a_s)^2 S_{bb} + 2(a_a - a_s)(a_b - a_s)S_{ab}$$

That is, the scattering function is absent of a solvent structure factor term!

4. (a) Show that if two identical polymers, “1” and “2”, (like Case I in your scattering notes), one with scattering power a_1 and the other with a_2 , are dissolved in a solvent “3”, the resulting $I(\mathbf{k})$ can be expressed as the sum of two groups of terms. The first is identical to the binary mixture result we obtained in class, and the other involves both P terms and Q terms for polymer-solvent correlations. Since the polymers are identical, $N_1 = N_2 = N$, and $N_3 = 1$ (because the solvent is a single small molecule). Also $P_1 = P_2 = P$, and there is no P for the solvent because remember that P measures correlations between scattering objects on a single chain. Finally, $Q_{11} = Q_{12} = Q_{22} = Q$, and $Q_{23} = Q_{13} = Q_s$. This scenario is possible in neutron scattering experiments, where one polymer has only H atoms, and the other has only D.
- (b) Furthermore, show that the second term can be made to vanish by use of a “zero-average-contrast” solvent, which could be obtained by mixing appropriate amounts of H- and D- containing solvent. Under these conditions, the experimental measurement of the form factor, P_{11} , can be readily conducted.

5. We have done all sorts of calculations for the scattered intensity function $I(\mathbf{k})$, with a bunch of results in terms of $P(\mathbf{k})$, the single-chain form factor. Not once though did we talk about what this function actually looks like. It turns out that its derivation isn't too involved and yields the well-known Debye scattering function.

What we need is the function $\langle \delta\rho(\mathbf{r})\delta\rho(\mathbf{r}') \rangle$. To calculate it, let's define the function as:

$$\begin{aligned}
 P(|\mathbf{r}-\mathbf{r}'|) &= \langle \delta\rho(\mathbf{r})\delta\rho(\mathbf{r}') \rangle \\
 &= \sum_{i=0}^N \sum_{j=0}^N \langle \delta\rho(\mathbf{r}_i, s_i) \delta\rho(\mathbf{r}_j, s_j) \rangle \cong \int_0^N ds \int_0^N ds' \langle \delta\rho(\mathbf{r}, s) \delta\rho(\mathbf{r}', s') \rangle
 \end{aligned}
 \tag{1}$$

where the sum-to-integral transformation is OK because N is presumed to be large.

$\langle \delta\rho(\mathbf{r}, s) \delta\rho(\mathbf{r}', s') \rangle$ may be interpreted as the probability of finding monomer s' at location \mathbf{r}' given that monomer s is at point \mathbf{r} .

- (a) To start, consider the Gaussian probability distribution $P(N, \mathbf{h})$ that was derived in class. This is the probability that monomer at $s' = N$ and $\mathbf{r}' = \mathbf{h}$ given that monomer $s = 0$ is at $\mathbf{r} = \mathbf{0}$. Write down the slightly modified expression you would need to evaluate $p(|\mathbf{r}-\mathbf{r}'|, |s-s'|)$, the probability that monomers separated by $|s - s'|$ along the chain contour are separated by $|\mathbf{r} - \mathbf{r}'|$ in space.
- (b) When we're finished we need to be in Fourier space. Transform your result in part (a) to the probability distribution $\hat{p}(\mathbf{k}, |s-s'|)$, *i.e.* the probability that monomers separated by $|s - s'|$ along the chain contour are related by wavevector \mathbf{k} .
- (c) Use the k -space probability distribution from (b) in the double integral of (1) to compute $P(\mathbf{k})$. Your result is called a Debye function. Make a plot of S/V vs. kR_g for a 50-50 blend of two

