Free Chains and Micelles of a Triblock Copolymer in Water

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Abstract

Small-angle neutron scattering (SANS) will be used to characterize the solution structure of a water-soluble triblock copolymer. At low temperature, the copolymer behaves as a polymer solution, but at higher temperature undergoes a transition and forms micelles. These micelles are capable of solubilizing hydrophobic materials and have found application in pharmaceuticals. You will learn all aspects of collecting a complete set of SANS measurements, including sample preparation, instrument setup, and the required measurements. After collecting your raw SANS data, you will learn how to correct and reduce the data into a form that can be analyzed. Data analysis will start with simple, model-independent methods, becoming more detailed and more realistic descriptions of the system. Guinier analysis, form factor scattering, and interparticle interactions will be considered.

1. Introduction

Block copolymers are polymer chains that have been carefully synthesized to have two or more "blocks" of repeating monomer units that are covalently bonded together. These polymer blocks can have a distinctly different chemical nature from each other, causing a competition of forces when the block copolymers are dissolved in a solvent, or even in a melt. This interplay of forces leads to a very rich array of microstructures that can form as dissimilar polymer blocks try to avoid each other, but forced to remain together through a covalent bond. Small-Angle Neutron Scattering (SANS) is a well-established method for characterizing the microstructure in various materials, including polymers. SANS measurements provide unique information that other techniques often cannot access, and thus SANS has had a major impact on the understanding of polymer conformations, morphology, rheology, and thermodynamics.[1] In this experiment, we will use SANS to quantify the

microstructural changes of a triblock copolymer in solution as the temperature of the solvent is changed.

The triblock copolymer that will be used for this study is a commercially available material, Pluronic P85.[2,3] These copolymers are block copolymers of propylene oxide (PO) and ethylene oxide (EO). The propylene oxide block is sandwiched between two ethylene oxide blocks. Typically, the ethylene oxide blocks are the same length. The structure of the polymer is shown in Figure 1.
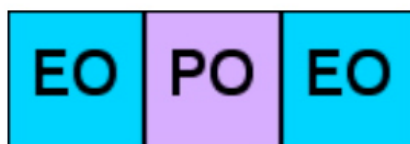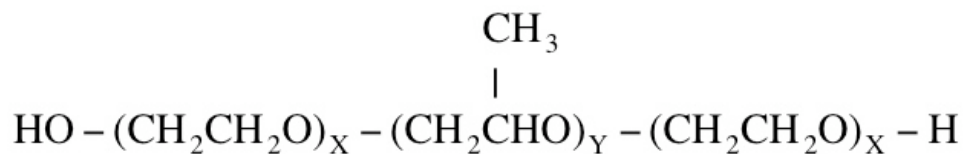
$$CH_3$$
$$|$$
$$HO-(CH_2CH_2O)_X-(CH_2CHO)_Y-(CH_2CH_2O)_X-H$$

Figure 1: Structure of Pluronic copolymers

Pluronic P85 has an average structure of $EO_{26}PO_{40}EO_{26}$, giving it an overall molecular weight of 4600 g/mol. The polymer is very soluble in water, forming gels at high concentrations (> 20 wt %) and temperatures above room temperature.

The objectives of the experiment are to:

Determine the dimensions of the free polymer chain in solution. Is the polymer chain in a Gaussian coil conformation, as it would be in a good solvent? This will be measured at low temperatures, where water is still a good solvent for both EO and PO blocks.

Determine the aggregation number of the micelles. At temperatures greater than room temperature, P85 molecules aggregate, as water becomes a poor solvent for the PO block. The size of the aggregate can be determined in several ways. It may be estimated from the radius of gyration, or from a more detailed model fit.

Determine the presence or absence of interparticle interaction effects. This will be done by identifying and analyzing deviations in the

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q-dependence of the scattering from the scattering expected for a non-interacting suspension of micelles.

2. Planning the Experiment

2.1 Scattering Contrast

In order for there to be small-angle scattering, there must be scattering contrast between, in this case, the polymer and the surrounding water. The scattering is proportional to the scattering contrast, $\Delta\rho$, *squared* where

$$\Delta\rho = \rho_p - \rho_w \qquad \leftarrow \text{Scattering Contrast}$$

and ρ_p and ρ_w are the **scattering length densities** (SLD) of the polymer and the water, respectively. Recall that SLD is defined as

$$\rho = \frac{\sum_{i=1}^{n} b_i}{V} \qquad \leftarrow \text{Scattering Length Density}$$

where V is the volume containing n atoms, and b_i is the (bound coherent) **scattering length** of the ith atom in the volume V. V is usually the molecular or molar volume for a homogenous phase in the system of interest. For a polymer chain, the monomer is a convenient reference volume.

The SLDs for the two phases in the present case, polymer and water, can be calculated from the above formula, using a table of the scattering lengths (such as reference [4]) for the elements, or can be calculated using the interactive *SLD Calculator* available at the NCNR's Web pages (http://www.ncnr.nist.gov/resources/index.html). From density measurements of Pluronic polymers in solution,[5] the molecular volume of each of the blocks can be calculated, and are found to be $V_o = 69.5$ Å^3 and $V_o = 82.4$ Å^3 for the EO and PO blocks, respectively. The SLD's for each of the polymer blocks and water (both H_2O and D_2O) are given below in Table 1. The average SLD of the whole Pluronic molecule is also calculated.

Table 1. The scattering length densities (SLD's) for the average Pluronic, its component blocks, and water.

Material	Chemical Formula	Mass Density (g/ml)	SLD (Å^{-2})
Average P85	$EO_{26}PO_{40}EO_{26}$	1.106	0.50×10^{-6}
EO	CH_2CH_2O	(see V_o above)	0.59×10^{-6}
PO	$CH(CH_3)CH_2O$	(see V_o above)	0.40×10^{-6}
Light water	H_2O	1.00	-0.56×10^{-6}
Heavy water	D_2O	1.105	6.36×10^{-6}

From Table 1 we see that scattering contrast for P85 in H_2O [proportional to $(0.50 - (-0.56))^2 = 1.12$] is 30 times smaller than in D_2O [$(0.5 - 6.36)^2 = 34.3$]. However, this is not the only factor to consider. One should also consider the concomitant incoherent scattering from each phase[1]. The incoherent scattering contributes an isotropic background that can obscure weak coherent scattering from the smaller structural features in a material. Here we are interested in both small-scale structure, on the order of the single polymer chain of ~ 1 nm, and much larger scale structure of the aggregates. Since the incoherent scattering from H_2O is about 30 times greater than that from D_2O, this also suggests that D_2O is the right choice for the solvent. The contrast in D_2O is much better and the lower incoherent scattering background will make it easier to distinguish the q-dependent coherent signal from the q-independent incoherent background.

2.2 Sample thickness to use

The next decision we face is: how thick should the sample be? Recall that the scattered intensity, $I_s(q)$, is proportional to the product of the sample thickness, d, and the sample transmission, T_s, where T_s, the ratio of the transmitted beam intensity to the incident beam intensity, is given by

$$T_s = e^{-\Sigma_t d}, \qquad \Sigma_t = \Sigma_c + \Sigma_i + \Sigma_a$$

where the total cross section per unit sample volume, Σ_t, is the sum of the coherent, incoherent and absorption cross sections per unit volume. The

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[1] Incoherent neutron scattering has no counterpart in x ray or light scattering. It arises from the interaction of the neutron with the nucleus, which is described by a scattering length that depends on the particular nuclear isotope and its nuclear spin state. For more information, see, for example, Ref. [6]

absorption, or neutron capture, cross section, Σ_a, can be computed accurately from the tabulated absorption cross sections of the elements (and isotopes) if the mass density and stoichiometry of the phase is known. Σ_a is wavelength dependent, being linearly proportional to λ for nearly all elements. The incoherent cross section, Σ_i, can be *estimated* from the cross section tables for the elements as well, but not as accurately, because it depends somewhat on the atomic motions and is, therefore, temperature dependent. The coherent cross section, Σ_c, can also only be estimated since it depends on the details of both the structure and correlated motion of the atoms in the material.

The computations involved in estimating sample transmission are straightforward but tedious. The task is made easier using the NCNR's Web-based *SLD Calculator* which computes not only scattering length density, but also estimates the incoherent and absorption cross sections per unit volume. Table 2 gives some of these results for P85, H_2O and D_2O.

Table 2. Macroscopic cross sections (i.e. cross sections per unit volume) computed with the *SLD Calculator* on the NCNR's Web site for the solute and solvents in the experiment. The values for the absorption cross sections are for a wavelength of 6 Å.

	Σ_c (cm^{-1})	Σ_i (cm^{-1})	Σ_a (6 Å) (cm^{-1})	Σ_t (cm^{-1})	$1/\Sigma_t$ (cm)
Average P85	0.351	5.19	0.0721	5.61	0.178
H_2O	0.260	5.37	0.0741	5.70	0.175
D_2O	0.518	0.136	0.000135	0.654	1.53

The sample to be measured consists of 10 % P85 (by weight) in D_2O, or approximately 10 % P85 by volume. Hence the total cross section per unit volume for the suspension is 0.90 (0.654 cm^{-1}) + 0.10 (5.61 cm^{-1}) = 1.15 cm^{-1}. The scattered intensity is proportional to $d \cdot \exp(-\Sigma_t d)$ which has a maximum at $d = 1/\Sigma_t$. This suggests an optimal sample thickness of $1/\Sigma_t$ = 0.87 cm. However, if Σ_i and Σ_a are small compared with Σ_t, d should be chosen to make T ~ 0.9 rather than 1/e = 0.37 to avoid multiple scattering. This is the case for our sample, so setting T = 0.9 corresponds to d = 0.09 cm. We will use a 1 mm path length cell for the measurement.

2.3 Estimate the Q-range

The basic building block of our sample is the polymer chain. Since we expect to see free chains in solution, we need to estimate this length scale. We also need an estimate of the micelle dimensions, so that we can measure over an appropriate q-range. The radius of gyration of a Gaussian polymer chain made of N monomer units is:

$$R_g^2 = \frac{N\ell^2}{6}$$

with the statistical segment length, l. The statistical segment length is the length for which the polymer chain follows a random walk. Typical values for l are 3.6 Å to 5 Å, depending on the chemical nature of the polymer. Using an estimated value of l = 4 Å, $R_g \sim$ 16 Å. An appropriate instrumental q-range to measure the polymer chains would have a q_{min} of approximately $q_{min} \sim 1/R_g \sim$ 0.06 Å^{-1} and a q_{max} of approximately $q_{max} \sim 1/l \sim$ 0.25 Å^{-1}

We expect at high temperatures, the polymer will aggregate and form structures larger than the size of an individual coil, so we will want to measure at smaller q-values to capture this larger length scale. Aggregation numbers (N_{agg}) can be of the order of 40 to 50 chains per micelle, or a corresponding spherical radius of $\sqrt[3]{N_{agg}} \approx 4$ times larger. So we will also configure the SANS instrument to measure at a minimum q of $q_{min} < 1/(4R_g) < 0.012$ Å^{-1}. Your mileage may vary. For unknown samples, you will need to look critically at the scattering (try a few samples), and make some judgment about whether this is really the right q-range for your samples. Additionally, we want to measure to as large of a q-value as practical, to have a clear measure of the incoherent background, which becomes q-independent at "large enough" q-values.

If we plot the expected scattering from these structures, (using the Web tools or the Igor Analysis models) we have some idea of what to expect in the actual data. A plot of these structures is shown in Figure 2. The aggregate has been simplistically approximated as a sphere. An incoherent background of 0.06 cm^{-1} from the D_2O has been added to the model calculations to make a more realistic prediction of what the scattering might look like. Using H_2O as the solvent would add an incoherent background of approximately 1 cm^{-1}, and provide much poorer scattering contrast.
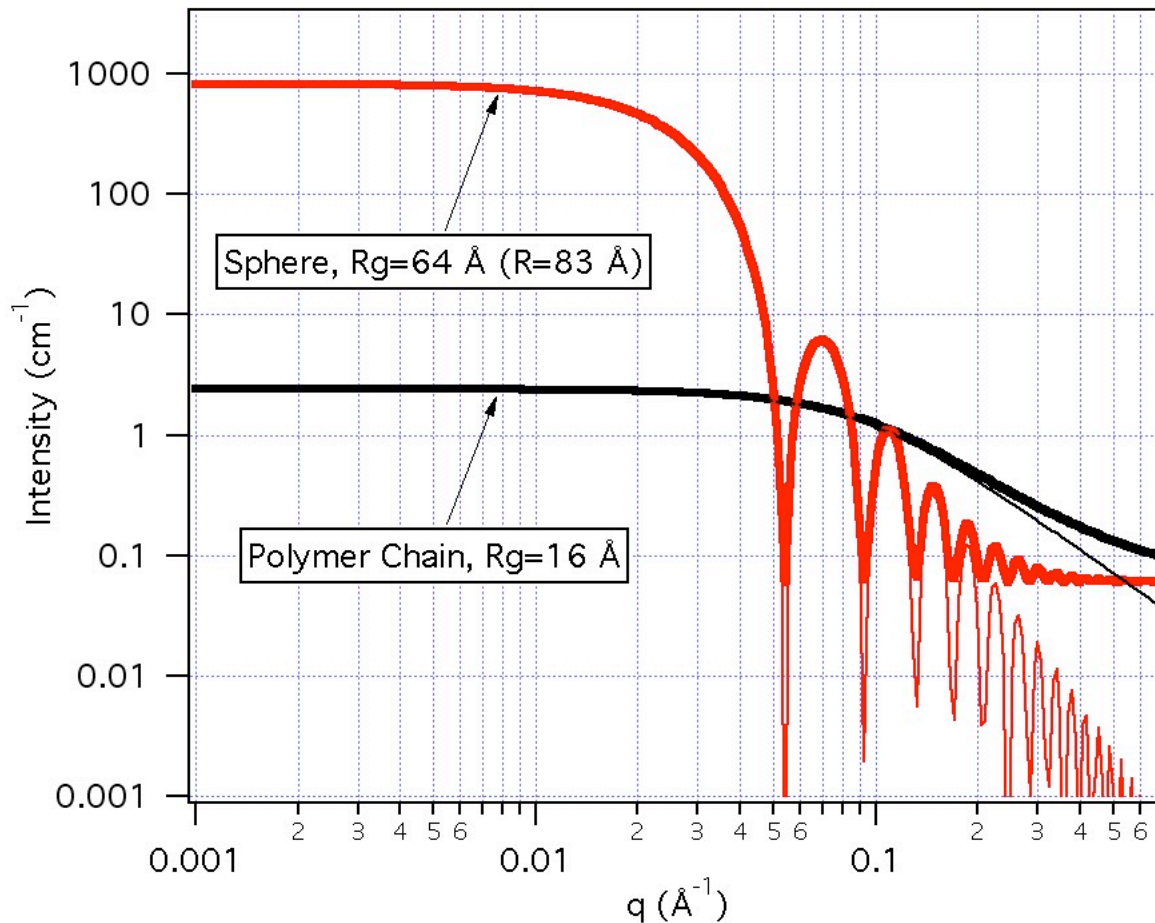
Figure 2: Predicted scattered intensity from a polymer chain and from a spherical particle. The thick model lines have an added incoherent background level that approximates D_2O.

3. Collecting the Data

3.1 Configuring the SANS instrument

Now that we know what q-range we would like to measure, we must decide how to configure the SANS instrument to do so efficiently. Here again we can use a computational tool, called SASCALC, as a guide. A schematic of the NCNR's 30-m SANS instrument is shown in Fig. 2, and the instrument configuration parameters, and their allowed range for the NG-3 30-m SANS instrument, are listed in Table 3.

Table 3. Instrument configuration parameters and their range of allowed values for the NG-3 30-m SANS instrument.[7]

| Variable	Allowed Range
Source:	neutron guide (NG3), 6 x 6 cm^2
Monochromator:	mechanical velocity selector with variable speed
Wavelength Range:	5 to 20 Å
Wavelength Resolution (FWHM):	10 to 30% wavelength spread
Source-to-Sample Distance:	3.5 to 15 m in 1.5 m steps via insertion of neutron guide segments
Sample-to-Detector Distance:	1.3 to 13.2 m continuously variable
Detector Offset:	0 – 25 cm (translation perpendicular to beam to extend the q-range covered at a given SDD)
Beam stop diameter:	2.54, 5.08, 7.62 or 10.16 cm
Beam Attenuator:	10 thicknesses to reduce beam intensity
Collimation:	circular pinhole collimation
Sample Size:	0.5 to 2.5 cm diameter
q range:	0.015 to 6 nm^{-1}
Size Regime:	1 to 600 nm
Detector:	64 x 64 cm^2 He-3 position-sensitive proportional counter (0.5 x 0.5 cm^2 resolution)
Unique feature:	neutron polarization
New Feature:	focusing lenses and gravity correction prisms
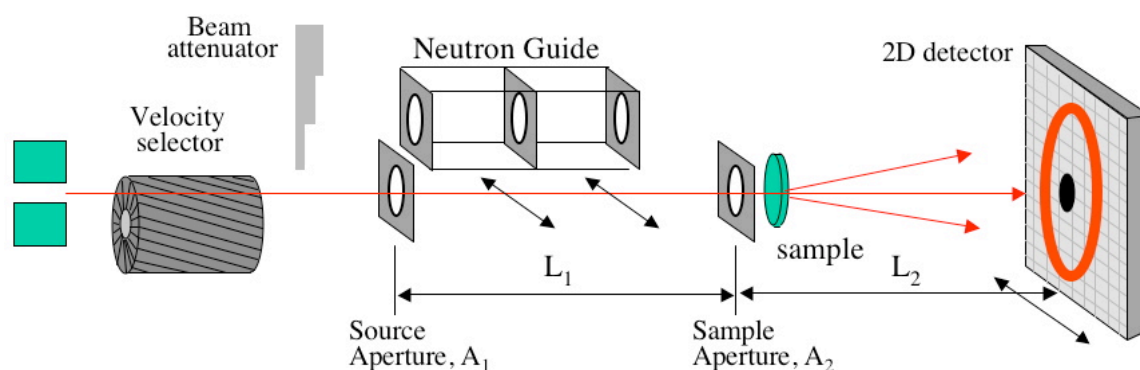
Figure 3. Schematic diagram of the components of the NCNR's 30-m SANS instruments.

For a given set of allowed parameters, SASCALC computes the corresponding q-range and the beam intensity (n/sec) on the sample. The q-range for a particular configuration is determined by the choice of wavelength, detector

distance and detector offset. To reach the large-q limit of the instrument, we must use the shortest available wavelength, 6 A, the shortest sample-to-detector distance, 133 cm, and the maximum detector offset, 25 cm. The number of neutrons guides affects primarily the beam intensity on the sample. In general, we choose the largest number of guides, to maximize the beam intensity on the sample, consistent with the desired q-range. For this large-q configuration, we can insert all 8 guides and still reach our desired q_{min} of 0.06 $Å^{-1}$. In this case, we have chosen to use 7 guides to avoid an excessive count rate on the detector, since this is a strongly scattering sample. The results from SASCALC for these choices are as follows:

```
Source Aperture Diameter =          5.00 cm
Source to Sample =                   542 cm
Sample Aperture to Detector =        138 cm
Beam diameter =                     3.01 cm
Beamstop diameter =                 2.00 inches
Minimum Q-value =                   0.0239 1/Å (sigQ/Q = 19.1 %)
Maximum Horizontal Q-value =        0.4211 1/Å
Maximum Vertical Q-value =          0.2467 1/Å
Maximum Q-value =                   0.4742 1/Å (sigQ/Q = 6.2 %)
Beam Intensity =                    5038230 counts/s
Figure of Merit =                   1.81e+08 Å^2/s
Attenuator transmission =           0.000286 = Atten # 8
*************** NG 3 ***************
Sample Aperture Diameter =            1.27 cm
Number of Guides =                    7
Sample Chamber to Detector =          133.0 cm
Sample Position is                    Chamber
Detector Offset =                     25.0 cm
Neutron Wavelength =                  6.00 Å
Wavelength Spread, FWHM =             0.150
Sample Aperture to Sample Position =  5.00 cm
```

Next, we consider how to configure the instrument to reach the low-q end of the desired measurement range. We want to reach $q_{min} < 0.01$ $Å^{-1}$ to measure the overall size of the micelles. We also want the q-range to overlap with the high-q configuration. The q-range and other parameters for this configuration is as follows, meeting our q_{min} requirement and providing good overlap with the high-q configuration in the q-range 0.024 $Å^{-1}$ to 0.042 $Å^{-1}$:

```
Source Aperture Diameter =          5.00 cm
Source to Sample =                  1472 cm
Sample Aperture to Detector =       1305 cm
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```
Beam diameter =                    7.17  cm
Beamstop diameter =                3.00  inches
Minimum Q-value =                  0.0035 1/Å (sigQ/Q = 30.3 %)
Maximum Horizontal Q-value =       0.0419 1/Å
Maximum Vertical Q-value =         0.0258 1/Å
Maximum Q-value =                  0.0491 1/Å (sigQ/Q = 6.5 %)
Beam Intensity =                   929371 counts/s
Figure of Merit =                  3.35e+07 Å^2/s
Attenuator transmission =          0.00602 = Atten # 6
**************** NG 3 ****************
Sample Aperture Diameter =                1.27 cm
Number of Guides =                        1
Sample Chamber to Detector =              1300.0 cm
Sample Position is                        Chamber
Detector Offset =                         20.0 cm
Neutron Wavelength =                      6.00 Å
Wavelength Spread, FWHM =                 0.150
Sample Aperture to Sample Position =   5.00 cm
```

3.2 What Measurements to Make

In addition to measuring the scattering from the sample for the two instrument configurations described in the previous section, additional measurements are needed to correct for "background." Counts recorded by the detector with the sample in place can come from 3 sources (see Figure 4): 1) neutrons scattered by the sample itself (the scattering we are interested in); 2) neutrons scattering from something other than the sample, *but which pass through the sample*; and, 3) everything else, including neutrons that reach the detector *without passing through the sample* (stray neutrons or so-called room background) and electronic noise in the detector itself. To separate these three contributions, we need three measurements:

i)   Scattering measured with the sample in place (which contains contribution from all 3 sources listed above), denoted I_{sam};

ii) Scattering measured with the empty sample holder in place (which contains contributions from the 2nd and 3rd sources listed above), denoted I_{emp}; and,

iii) Counts measured with a complete neutron absorber at the sample position (which contains only the contribution from the 3rd source listed above), denoted I_{bdg}.
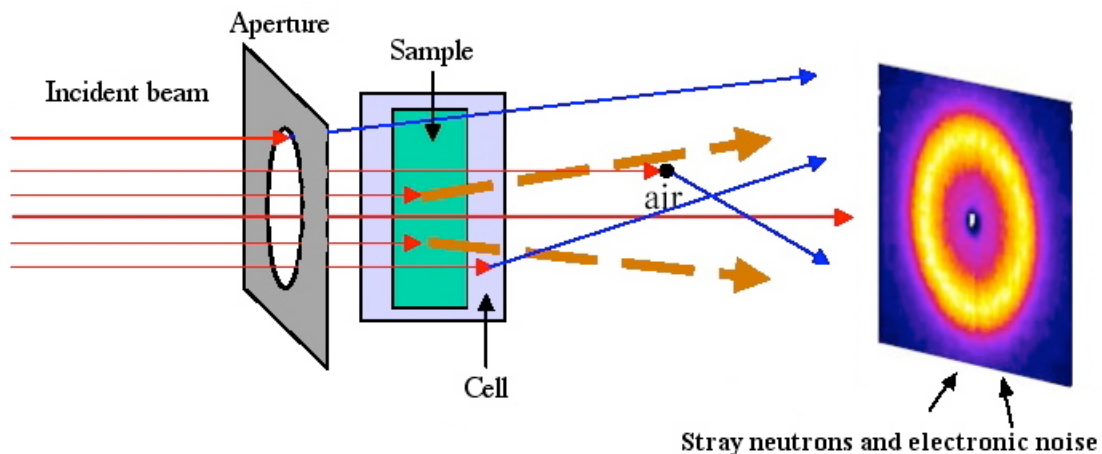
Figure 4: Sources of neutrons measured at the detector. Additional measurements must be made to correct the raw sample scattering to obtain data that represents scattering from only the sample.[8]

In addition to these three 'scattering' measurements, the transmission (the fraction of the incident beam intensity that passes through the sample without being scattered or absorbed) of the sample and the sample cell must also be measured in order to correctly subtract the contributions to the background and to calibrate the scattering on an absolute cross section scale (the procedure is discussed in Section 4, Data Reduction). The transmission is measured by inserting a calibrated attenuator in the incident beam (to reduce the direct beam intensity to an accurately measurable level) and measuring the direct beam intensity with and without the sample (or the sample cell) in position. The ratio of these two short measurements (typically 2-3 minutes each) is the sample (or sample cell) transmission.

How the scattering and transmission measurements are used to reduce the data to a quantity called the differential scattering cross section, which is intrinsic to the sample is described in Section 4, Data Reduction.

3.3 How long to count

A SANS experiment is an example of the type of counting experiment where the uncertainty, or more precisely the standard deviation, σ, in the number of counts recorded in time, $I(t)$, is $\sigma = \sqrt{I(t)}$. If the scattering is roughly evenly distributed over the SANS detector, then a good rule of thumb is that one should accumulate about 500,000 total detector counts per sample

measurement. If the accumulated counts are circularly averaged, one obtains about 50 data points when plotting I(q) versus q. This amounts to about 10,000 counts per data point with a standard deviation of $\sqrt{10,000} \sim 100$ or an uncertainty of about 1 %, which is good enough for most purposes.
A related question is how long should the background and empty cell measurements be counted relative to the sample measurement. The same $\sigma = \sqrt{I(t)}$ relationship leads to the following approximate result for the optimal relative counting times

$$\frac{t_{background}}{t_{sample}} = \sqrt{\frac{Count\,Rate_{background}}{Count\,Rate_{sample}}}.$$

Hence if the scattering from the sample is weak, the background should be counted for as long (but no longer!) as the sample scattering. However, if the sample scattering count rate is, say, 4 times greater than the background rate, the background should be counted only half as long as the sample scattering.

4. Data Reduction

The scattered intensity I(q) is related to the absolute cross-section $d\Sigma(q)/d\Omega$ by the expression:

$$I(q) = \phi\ A\ d\ T\ (d\Sigma(q)/d\Omega)\ \Delta\Omega\ \varepsilon\ t$$

where
ϕ = flux on the sample,
A = sample area,
d = sample thickness,
T = measured sample transmission,
$\Delta\Omega$ = solid angle subtended by one pixel of the detector,
ε = detector efficiency, and
t = effective counting time, which is renormalized to give 10^8 monitor counts.

From this expression, one can observe that increasing either the sample area or sample thickness increases the scattered intensity.

The three measurements needed to determine the scattering from the sample are the **sample, empty beam and blocked beam**. These three **raw data measurements** are defined as follows:

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$$I_{SAM} = C_O \, T_{sample+cell} \left(\left(\frac{d\Sigma(q)}{d\Omega} \right)_{sample} + \left(\frac{d\Sigma(q)}{d\Omega} \right)_{Empty\,Beam} \right) + I_{Blocked\,Beam},$$

$$I_{EMP} = C_O \, T_{cell} \left(\frac{d\Sigma(q)}{d\Omega} \right)_{Empty\,Beam} + I_{Blocked\,Beam}, \text{ and}$$

$$I_{BGD} = I_{Blocked\,Beam}$$

where I is the measured intensity and T is the measured transmission. C_o is given by $C_o = \phi \, A \, d\Delta\Omega \, \varepsilon \, t$.

The raw SANS data are corrected for the empty beam and blocked beam contributions using

$$I_{COR} = (I_{SAM} - I_{BGD}) - \left(\frac{T_{sample+cell}}{T_{cell}} \right)(I_{EMP} - I_{BGD})$$

to obtain the scattering contribution arising only from the sample. This corrected sample scattering is further corrected to account for any differences in detector sensitivity (~1%) from pixel to pixel. The instrument scientists measure the detector sensitivity each reactor cycle using an isotropic scattering material such as Plexiglas or water. The correction is made by dividing the corrected sample scattering by the detector sensitivity, normalized to 1.0 count per pixel, on a pixel-by-pixel basis. This can be written as

$$I_{CAL} = \frac{I_{COR}}{\text{Normalized Detector Sensitivity}} = \phi \, A \, d \, T_{sample+cell} \left(\frac{d\Sigma(q)}{d\Omega} \right)_{sample} \Delta\Omega \, \varepsilon \, t$$

The data represents the number of neutron counts scattered from the sample, and depends on the instrumental conditions. In order to obtain the differential scattering cross-section of the sample, $\frac{d\Sigma(q)}{d\Omega}$, in absolute units of cm^{-1}, the data must be put on an absolute scale by one of two methods: 1) the direct beam flux method or 2) the standard sample method. To use the direct beam flux method, measure a direct beam with nothing in the beam except an attenuator.

Then, $I_{Direct} = \phi \, A \, T_{atten.} \, \Delta\Omega \, \varepsilon \, t$. The data are then put on an absolute scale using the relation:

$$\left(\frac{d\Sigma(q)}{d\Omega}\right)_{sample} = \left(\frac{I(q)_{CAL}}{I_{Direct}}\right)\left(\frac{1}{d}\right)\left(\frac{T_{atten.}}{T_{sample+cell}}\right).$$

Alternatively, to use the standard sample method, a sample with known absolute scattering cross-section at q=0, $\dfrac{d\Sigma(q=0)}{d\Omega}$, must be measured in exactly the same instrument configuration as used for the experiment. Instrument scientists have previously determined $\dfrac{d\Sigma(q=0)}{d\Omega}$ for several standard samples that are available for use. The measured intensity at q=0 for the standard sample given by

$$I(q=0)_{STD} = \phi \, A \, d_{STD} \, T_{STD+cell} \left(\frac{d\Sigma(q=0)}{d\Omega}\right)_{STD} \Delta\Omega \, \varepsilon \, t.$$ The data are then put on an absolute scale using the relation:

$$\left(\frac{d\Sigma(q)}{d\Omega}\right)_{sample} = \left(\frac{I(q)_{CAL}}{I(q=0)_{STD}}\right)\left(\frac{d_{STD}}{d}\right)\left(\frac{T_{STD+cell}}{T_{sample+cell}}\right)\left(\frac{d\Sigma(q=0)}{d\Omega}\right)_{STD}.$$

These corrections and absolute scaling are made within the user-friendly data reduction software package that uses IGOR.

5. Data Analysis

5.1 Guinier Approximation
The reduced SANS data will be modeled by progressively more realistic (and more complex) models.[5,9] The greatest benefits from the simple models are that they are easy to do, and require no assumptions about the actual shape of the object. The scattering from dilute objects, at small enough q-values, can be approximated by a simple exponential decay:

$$I(q) \approx I(0)\exp\left(-\frac{1}{3}q^2R_g^2\right)$$

So a plot of ln[I(q)] vs. q^2 will be linear, and the slope will be negative, and proportional to the radius of gyration of the object. This type of plot is called a Guinier plot, and works for any shape object. It is valid in a q-range of approximately $qR_g \leq 1$.

To Do: Fit the data from a dilute solution to the Guinier approximation (data from micelles of 1 % by weight P85 in D_2O will be provided for you to use). Determine the R_g of the polymer in solution, and the R_g of the aggregate at a function of temperature. How does the R_g of the micelle change with temperature? What happens when you measure the R_g of the 10 % P85 micelles?

5.2 Gaussian chains in solution
The polymer chains in solution should behave like Gaussian coils, and their scattering should be well-described by a Debye function:

$$I(q) = \phi(\Delta\rho)^2 Z v_m \frac{2(e^{-x} + x - 1)}{x^2}$$

Z is the degree of polymerization, v_m is the specific volume of the monomer, and $x = (qR_g)^2$.

To Do: Fit the pre-micellar data (at low temperatures) with both the Debye function and a Guinier fit. Compare the results to our rough estimate of the polymer size. If there are differences, what could be the reasons?

5.3 Core – Shell Micelles
For a more detailed analysis of the scattering, we need to postulate a structure for the aggregate. The structure of the P85 micelles is expected to be like Figure 5, where the insoluble PPO blocks cluster together and are surrounded by a shell of the soluble PEO chains, much like a polymer brush. From a distance, the aggregate is simply a sphere. Closer up, it is a spherical core, with a shell on the surface. We will consider our solution to contain some concentration of these micellar structures, with a "dry" core that contains only polymer, and a shell that contains extended chains and some quantity of solvent.
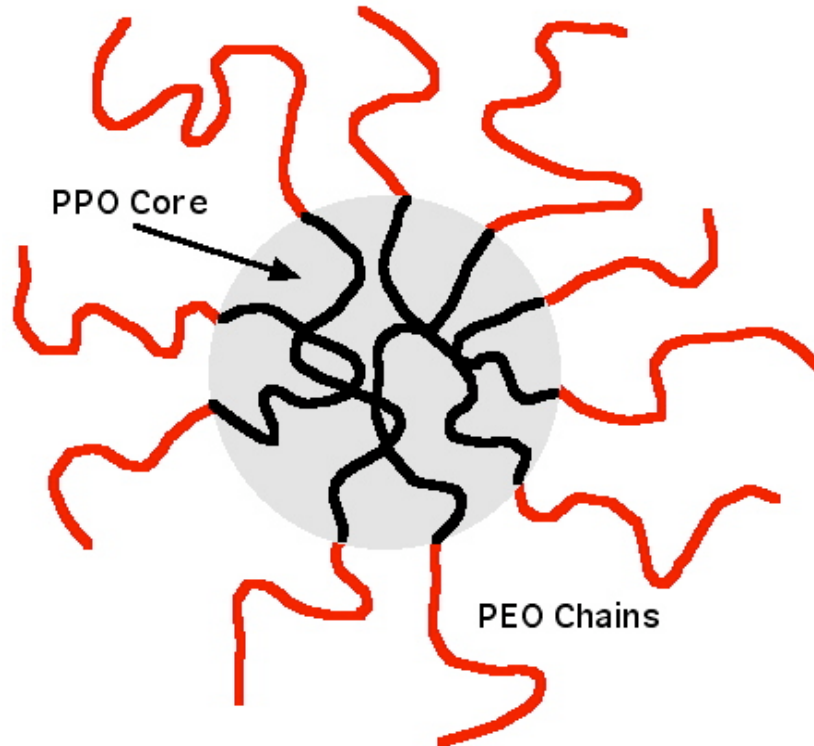
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Figure 5: Schematic structure of a P85 micelle. The insoluble PPO blocks are expected to be in the core, surrounded by extended PEO chains that remain soluble in water.

The scattered intensity from a collection of monodisperse particles can be written as:

$$I(q) = n_p P(q) S(q)$$

where n_p is the number density of particles, $P(q) = f^2(q)$ is the form factor, and $S(q)$ is the structure factor. The scattering amplitude is defined as a Fourier integral of the scattering length density difference between any point in the particle and the solvent:

$$f_k(\vec{q}) = \int_{\text{particle } k} \left[\rho_k(\vec{r}) - \rho_{solv} \right] e^{i\vec{q}\cdot\vec{r}} d\vec{r}$$

For the case of a core-shell sphere:

$$P(q) = \left[\frac{3V_c(\rho_c - \rho_s) j_1(qR_c)}{qR_c} + \frac{3V_s(\rho_s - \rho_{solv}) j_1(qR_s)}{qR_s} \right]^2$$

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where R_c is the core radius, R_s is the outer radius of the shell (the total radius of the sphere), $j_1(x) = (\sin x - x \cos x)/x^2$, and $V_i = (4\pi/3)R_i^3$. Note that the form factor contains all of the information about the shape and scattering contrast of the particle. The structure factor, S(q), describes the relative positions of the micelles in solution. If the solution is dilute, the micelles do not interact with each other (think of an ideal gas of micelles), then the structure factor, S(q) = 1 for all q-values. As the solution becomes more concentrated, the micelles "feel" the presence of each other, excluding the volume of solution that other micelles can occupy. This is reflected in the relative positions of the micelles in the solution. S(q) is related to the pair correlation function, g(r), which becomes more oscillatory in nature as the micelles become more concentrated and more constrained to be in a particular location in the solution (think of the extreme case of a crystal). Our system is between these extremes of concentration. We will use the simplest S(q), calculated for a hard-sphere fluid.[10,11]

We expect from thermodynamics that the aggregation number will not be a single value, but rather a distribution. This polydispersity in micelle size has been incorporated into the model calculation by integrating the form factor over a distribution of core radius. The distribution used here is a Schulz distribution, very similar to a Gaussian. Calculating the scattered intensity for polydisperse, interacting particles, is in general a difficult problem. The simple form for the scattered intensity I(q) = n P(q) S(q) relies on the assumption that all of the particles are identical. In a polydisperse system, this is not the case – each particle size (and the unknown size of the neighboring particle) must be explicitly taken into account. The mathematics quickly becomes tedious, if not intractable. See the references and Appendix C for all of the details [8,9]. For this model, the form factor is averaged over the size distribution, while the structure factor is approximated as calculated for the mean size. This approximation is very good for the particle density and interactions between the micelles.

To Do: Fit the scattered intensity from 10 % P85 to a model of core-shell spheres with hard sphere interactions. If the fit is not good at some temperatures, what part of the physical structure of the micelles has not been incorporated in the model? How would the model compare to the data if there were no interparticle interactions? If the fit is good, what do the parameters mean? Do they make any physical sense? How could the model be improved?

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Appendix A: Dry Core - Shell Model of micelles
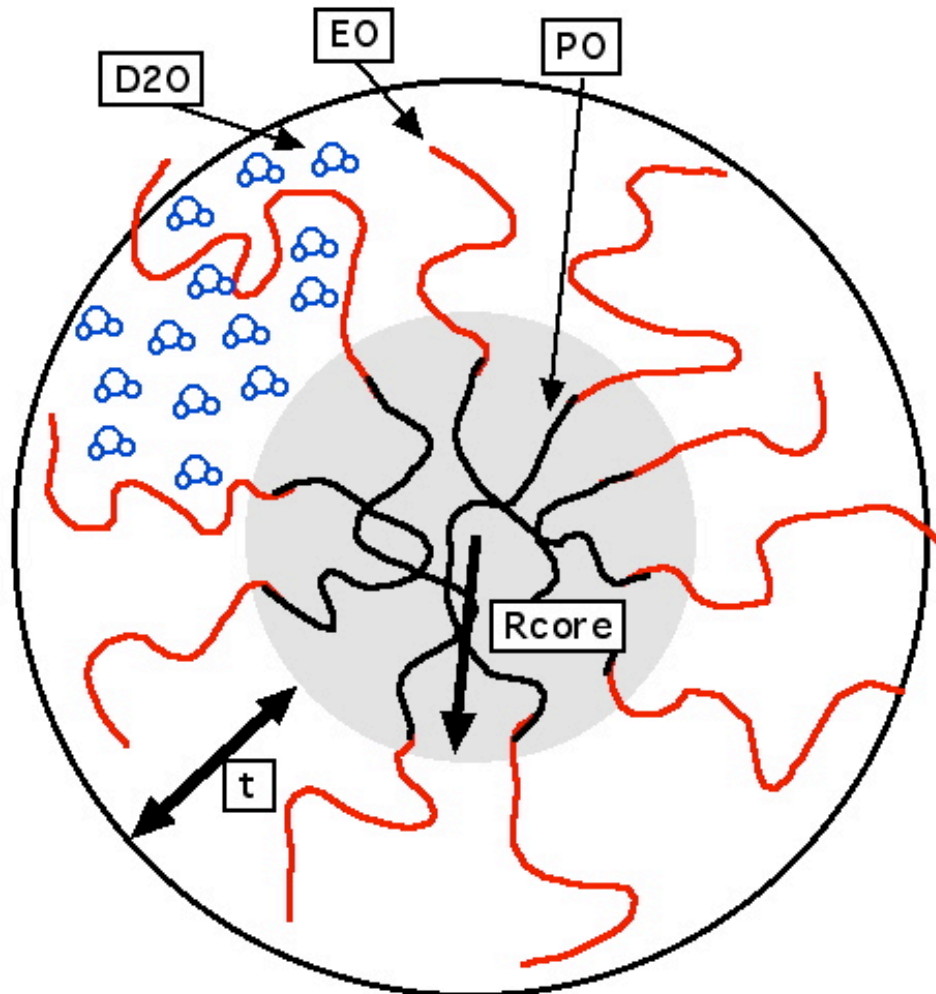
The dry core and shell model we are using to fit the data gives us several parameters:

    1) The core radius, R_c

    2) The shell thickness, t

    3) The core scattering length density, ρ_c

    4) The shell scattering length density ρ_s

    5) The polydispersity of the core radius

    6) The effective volume fraction of micelles

So what do all of these parameters mean?

Let's start with (5), the polydispersity. This is defined as $p = \sigma / R_{avg}$, or the standard deviation of the distribution divided by the mean radius. Values of p=0.1 to p=0.5 are quite typical for colloidal systems. For the calculations that follow, we will use only the average core radius. A more accurate calculation must account for the size distribution ($V_{avg} \neq \frac{4\pi}{3} R_{avg}^3$). See [Chen and Lin] for an example.

The effective volume fraction, (6), is the volume fraction of micelles in the sample *as they interact with each other as hard spheres*. This is not the same as the physical volume fraction. For 10 wt % P85, this is very close to a volume fraction of 0.10. The effective spherical radius of each micelle is larger than just the polymer content, since the shells are swollen with water. So the volume fraction of the solution that the micelles exclude from each other, is significantly larger than 10%.

The physical dimensions (1-2) and the scattering lengths (3-4) are intertwined. They must be connected through a complete material balance. We can work out this accounting to determine the (average) aggregation number of the micelles. For the diagram above of our "dry core" micelle:

Each micelle contains some number of chains, N_{agg}
Each micelle contains some number of water molecules
The core contains all of the PO, and no water
The core may contain some fraction of the EO (f)
The shell contains EO and some D_2O (y = moles D_2O /moles EO)

The following material balances must then hold true:

$$V_{core} = \frac{4\pi}{3} R_c^3 = N_{agg} \cdot 40 \cdot v_{PO} + N_{agg} \cdot 52 \cdot f \cdot v_{EO}$$

$$V_{shell} = \frac{4\pi}{3} \left[(R_c + t)^3 - R_c^3 \right]$$
$$= N_{agg} \cdot 52 \cdot (1 - f) \cdot v_{EO} + N_{agg} \cdot 52 \cdot (1 - f) \cdot y \cdot v_{D2O}$$

These equations state that the core is made up of the volume of all 40 of the PO segments on each of N_{agg} chains, plus some fraction, f, of the (2*26=52) EO segments. The shell volume is the fraction of EO (1-f) that is not in the core,

plus some molar ratio of D_2O that completes the volume. V_{D2O} is the molar volume of D_2O. The SLD of the core was held fixed during the fitting at the value calculated for PO (which is hardly different than EO). The shell SLD was allowed to vary, and (should have) arrived at an optimal SLD somewhere between the SLD of the core and the SLD of D_2O. The SLD of the shell is an average over all of the EO and D_2O in the shell volume, or more simply, the sum of the scattering lengths of everything in the shell divided by the volume they occupy:

$$\rho_{shell} = \frac{N_{agg} \cdot 52 \cdot (1-f) \cdot \sum b_{EO} + N_{agg} \cdot 52 \cdot (1-f) \cdot y \cdot \sum b_{D2O}}{N_{agg} \cdot 52 \cdot (1-f) \cdot v_{EO} + N_{agg} \cdot 52 \cdot (1-f) \cdot y \cdot v_{D2O}}$$

Where $\sum b_{EO}$ is the sum of scattering lengths of the EO unit:

$$\sum b_{EO} = [2(6.646) + 4(-3.739) + 5.803] fm \cdot \frac{\mathring{A}}{10^5 \, fm} = 4.139 \cdot 10^{-5} \mathring{A}$$

and $\sum b_{D2O}$ is the sum for D_2O:

$$\sum b_{D2O} = [2(6.67) + 5.803] fm \cdot \frac{\mathring{A}}{10^5 \, fm} = 19.14 \cdot 10^{-5} \mathring{A}.$$

Since the SLD of the shell is a fitted parameter, and everything else in the equation is known, y can be solved for directly as:

$$y = \frac{\sum b_{EO} - \rho_{shell} \cdot v_{EO}}{\rho_{shell} \cdot v_{D2O} - \sum b_{D2O}}$$

As an example, the 10 % P85 sample at 40 C should yield values of:
    Rc = 40.4 Å
    t = 30.1 Å
    SLD shell = 5.78E-6 Å^{-2}

    y is directly calculated as y = 22, meaning that there are 22 D_2O molecules per EO unit in the shell. The two material balances can be solved for N_{agg} and f:

$$N_{agg} = \left(\frac{V_{shell}}{52(v_{EO} + y \cdot v_{D2O})} + \frac{V_{core}}{52 v_{EO}} \right) \Bigg/ \left(1 + \frac{40 v_{PO}}{52 v_{EO}} \right)$$

and

$$f = \frac{\frac{4\pi}{3} R_c^3 - N_{agg} \cdot 40 v_{PO}}{N_{agg} \cdot 52 v_{EO}}$$

with the volumes:

$$V_{shell} = \frac{4\pi}{3}\left[(R_c + t)^3 - R_c^3\right]$$

$$V_{core} = \frac{4\pi}{3} R_c^3$$

Plugging in the values gives:

$N_{agg} = 56$

$f = 0.44$

indicating that there are about 56 P85 molecules per micelles and that there is a significant fraction of EO units in the "dry" core of the micelle.

• For each of the temperatures, does the aggregation number change at the same rate as the overall radius of the micelle? What does this say about the water content of the micelle as a function of temperature?

• What if we change the assumption that the core is "dry" and instead contains some D_2O? Why would there be D_2O in the core with EO and PO? How many additional parameters do we need, and how would we solve for them? How could we determine which set of assumptions is more correct?

As a final note, the core-shell model could be written such that the aggregation number and EO fraction are the "fitting" parameters, and the radii are calculated internally with volumes specific to P85. The core-shell model is then more convenient for determining the parameters we want, but with a loss of generality. Also, the details of the assumptions and material accounting are hidden, and not subject to critical thought.

Appendix B: A Sphere with "Whiskers"

The core-shell model we used is not very realistic, since the SLD's are not uniform slabs, but made of Gaussian chains. A more realistic approach is to treat the micelles as aggregates of polymer chains, with all of the PPO confined to the core of the micelle. To calculate the form factor of such a structure, several terms must be determined:

1) The self-correlation of the sphere
2) The self-correlation of the chains
3) The cross correlation between the sphere and the chains
4) The cross correlation between different chains

The scattering from a single micelle, its form factor, is thus a sum of four terms. The explanation of each of the terms closely follows work in the literature.[12] The self-correlation of the spherical core of radius R is given by:

$$F_s(q,R) = \Phi^2(q,R) = \left\{ \frac{3[\sin(qR) - qR\cos(qR)]}{(qR)^3} \right\}^2$$

and is also a function of the magnitude of the scattering vector, q. The PEO chains of the shell obey Gaussian statistics, and so their self-correlation is given by the Debye function:

$$F_c(q,L,b) = \frac{2[\exp(-x) - 1 + x]}{x^2}$$

Where $x = R_g^2 q^2$ and R_g is the radius of gyration of the polymer chain. A polymer chain of contour length, L, and Kuhn length, b, has a radius of gyration, $R_g^2 = Lb/6$. The contour length of a chain is the total extended length of the chain. The Kuhn length, or the statistical segment length is related to the flexibility of the monomer units of the chain. The cross term between the sphere and the Gaussian chains at the surface of the sphere is:

$$S_{sc}(q) = \Phi(q,R)\,\psi(q,L,b)\frac{\sin(qR)}{qR}$$

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where the function $\psi(q,L,b)$ is the form factor amplitude of a single chain:

$$\psi(q,L,b) = \frac{1 - \exp(-x)}{x}$$

where $x = R_g^2 q^2$ as before. The final term is the interference between chains, calculated as integrations over two chains and over the distance distribution of the starting points of the two chains:

$$S_{cc}(q) = \psi^2(q,L,b)\left[\frac{\sin(qR)}{qR}\right]^2$$

Now the total forma factor of one micelle can be calculated. For a micelle with aggregation number N_{agg}, and total excess scattering length of the polymer blocks are ρ_s in the spherical core and ρ_c in the surrounding chains, then adding up the four terms gives:

$$F_{mic}(q) = N_{agg}^2\rho_s^2 F_s(q,R) + N_{agg}\rho_c^2 F_c(q,L,b) +$$
$$N_{agg}(N_{agg} - 1)\rho_c^2 S_{cc}(q) + 2N_{agg}^2\rho_s\rho_c S_{sc}(q)$$

The forward scattering (q = 0) has a particularly simple form:

$$F_{mic}(q = 0) = N_{agg}^2(\rho_s + \rho_c)^2$$

The model can be made more realistic by including more features, with an according increase in the complexity of the calculation and increase in the number of fitting parameters.[13]. Other "improvements" that can be added to the "whisker" model are:

   1) Polydispersity of the aggregation number
   2) Interparticle interference from micelle-micelle interactions
   3) Rough interface between PO core and EO shell
   4) Prevent EO chains from freely penetrating the PO core

You will have to judge whether these additions are appropriate (physically), and whether there is a significant gain in understanding of the system derived from the increased complexity.

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Appendix C: Polydisperse Dispersions

C.1 Basic Equations

In a colloidal dispersion, there are typically discrete particles of different atomic composition from the surrounding solvent. It is then convenient to divide the scattering volume into N_p cells, each containing one particle and structureless solvent.

The scattered intensity from a collection of discrete particles can be written as:[14]

$$\frac{d\Sigma}{d\Omega}(\vec{q}) = \frac{1}{V}\sum_{k=1}^{N_p}\left\langle \left|f_k(\vec{q})\right|^2\right\rangle + \frac{1}{V}\left\langle \sum_{k=1}^{N_p}\sum_{\substack{j=1\\ j\neq k}}^{N_p} f_k(\vec{q})f_j^*(\vec{q})e^{i\vec{q}\cdot(\vec{r}_k-\vec{r}_j)}\right\rangle$$

(C.1)

where $\vec{r}_k$ and $\vec{r}_j$ are the centers of mass of cells k and j respectively. The scattering amplitude is given as a Fourier integral of the distribution of scattering centers within each cell,

$$f_k(\vec{q}) = \int_{\text{particle k}}\left[\rho_k(\vec{r}) - \rho_{solv}\right]e^{i\vec{q}\cdot\vec{r}}d\vec{r}$$

(C.2)

The scattering amplitude of a cell depends only on the spatial arrangement of nuclei in the cell, and on the relative scattering length difference between particle and solvent. For the special case of monodisperse spherical particles, $f_k(\vec{q}) = f_j^*(\vec{q}) = f(q)$, and Equation C.1 can be factored into the form:

$$\frac{d\Sigma}{d\Omega}(\vec{q}) = n_p\left\langle\left|f(q)\right|^2\right\rangle\left\{1 + \left\langle\sum_{k=1}^{N_p}\sum_{\substack{j=1\\ j\neq k}}^{N_p}e^{i\vec{q}\cdot(\vec{r}_k-\vec{r}_j)}\right\rangle\right\}$$

(C.3)

where n_p is the number density of particles. This is compactly represented as

$$\frac{d\Sigma}{d\Omega}(\vec{q}) = n_p P(q) \cdot S(\vec{q})$$

(C.4)

by identifying the bracketed term as the form factor, P(q), and the term in parentheses as the structure factor, $S(\vec{q})$.

The structure factor contains all of the information about the spatial arrangement of the particles relative to an arbitrary origin. For the case of an isotropic solution (which will be the only one of interest in this Appendix), the average can be calculated around a centrally located sphere. The orientational average can be calculated as:

$$S(q) = 1 + 4\pi n_p \int_0^\infty \left[g(r) - 1\right] \frac{\sin qr}{qr} r^2 dr$$

(C.5)

The pair correlation function, g(r), can be calculated using liquid state theory, and thus the structure factor can be calculated. The pair correlation function can be related to thermodynamic properties of the fluid such as pressure or compressibility.[15]

To obtain information from systems of interacting colloids, it is necessary to model the scattered intensity by calculating the form and structure factors. This is easily done for monodisperse, spherical particles. However, real colloidal dispersions are not monodisperse, and not always spherical. The following sections describe the approximations that can be used to treat the scattering from polydisperse populations, and special cases that can be treated without approximation.

C.2   Structure Factors

The effect of interactions between particles - even excluded volume interactions - must be taken into account when interpreting the scattered

intensity. For particles of known morphology, it is often desirable to determine the unknown interparticle potential. This is done by proposing an interaction potential, using statistical mechanics to calculate S(q), and fitting the model to the data.

The interparticle potential determines the equilibrium arrangement of particles, g(r), from which S(q) can be calculated. For a homogeneous, isotropic fluid of spheres, the Ornstein-Zernicke equation is:[15]

$$h(r) = g(r) - 1 = c(r) + n \int c(|\vec{r} - \vec{x}|) h(x) d\vec{x} \qquad \text{(C.6)}$$

and states that the total correlation, h(r), between two particles is the sum of the direct correlations, c(r), and the sum of all other correlations which are felt indirectly through all other particles. The structure factor S(q) depends directly on c(r) (compare Equations C.5 and C.6). Unfortunately, c(r) and h(r) are both unknown functions, and the Ornstein-Zernicke equation can only be solved if there is available an additional relation between them. This additional equation is an approximation, called a closure relation, which relates h(r) and c(r).

The simplest of these closure relations is the Percus-Yevick closure,[16]

$$c(r) = g(r)\left[1 - e^{\beta u(r)}\right] \qquad \text{(C.7)}$$

which provides a good description of fluids with very short ranged interactions. For the simplest case of hard sphere interactions:

$$U(r) = \begin{cases} \infty & r \leq \sigma \\ 0 & r > \sigma \end{cases} \qquad \text{(C.8)}$$

c(r) is identically zero for $r > \sigma$. In this case, an analytic solution for the structure factor can be found.[17,18]

C.3 Polydisperse Colloids

Up to this point, the discussion of form and structure factors has been limited to the simplest, but unrealistic, case of monodisperse particles. Real colloidal dispersions are polydisperse, and contain p different-sized components. To properly treat a general p-component mixture greatly complicates the analysis of SANS data, and can quickly make the problem intractable if simplifying approximations are not made. Care must be taken that any approximations are appropriate.

For a p-component mixture of spheres, the scattered intensity takes a slightly more complicated form than Equation C.4:[19]

$$\frac{d\Sigma}{d\Sigma}(q) = \sum_i^p \sum_j^p \left(n_i n_j\right)^{\frac{1}{2}} f_i(q) f_j(q) S_{ij}(q)$$

(C.9)

but still retains the same essential features as the monodisperse form. The scattered intensity is proportional to the concentration of scatterers, n_i, the scattering amplitudes, $f_i(q)$, and now also the partial structure factors, defined by:

$$S_{ij}(q) = \delta_{ij} + 4\pi\left(n_i n_j\right)^{\frac{1}{2}} \int \left[g_{ij}(r) - 1\right] \frac{\sin qr}{qr} r^2 dr$$

(C.10)

which are the Fourier representation of the arrangement of spheres of type j around a centrally located i particle. d_{ij} is the Kronecker delta, and equals one if i = j, and is zero otherwise. For p components, $p(p+1)/2$ independent partial structure factors are necessary to describe the microstructure. These are related to the partial pair correlation functions, $g_{ij}(r)$ through the set of multicomponent Ornstein-Zernicke equations:[22]

$$h_{ij}(r) = c_{ij}(r) + \sum_k^p n_k \int c_{ik}\left(|\vec{r} - \vec{x}|\right) h_{kj}(x) d\vec{x}$$

(C.11)

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which now require a set of closure relations to relate the $h_{ij}(r)$ to the $c_{ij}(r)$. This set of equations has only been solved in closed form for hard sphere mixtures. It has been solved for continuous Schulz-distributed spheres in the PY approximation.[21,22] Interaction potentials other than hard spheres require different, more appropriate closure relations, and the set of Ornstein-Zernicke equations must be solved numerically for the partial structure factors. Particles that are not spherical add a further level of complexity since the spherical symmetry is lost. In these systems, the relative position *and* orientation of the particles is necessary to fully specify the state of the dispersion.

C.4 Approximations

If the particle sizes and orientations are uncorrelated, the scattered intensity can be written in a familiar form,[23,24]

$$\frac{d\Sigma}{d\Omega}(q) = n_p P(q) S'(q) \qquad (C.12)$$

with the following definitions for the average form factor:

$$P(q) = \overline{f^2(q)} \qquad (C.13)$$

and the effective structure factor:

$$S'(q) = 1 + \left(\frac{\overline{f(q)}^2}{\overline{f^2(q)}} \right) [S(q) - 1] = 1 + \beta(q)[S(q) - 1] \qquad (C.14)$$

where S(q) is the one component structure factor for the average radius. The horizontal bars represent an average over the size distribution. This "decoupling" approximation is appropriate for repulsive interaction and moderate polydispersity (<20%). For hard sphere or attractive interactions, there are significant deviations from the exact solution, especially at low q.[14,22] A second, better approximation is the average structure factor approximation,[25] where the scattered intensity is factored into the form:

$$\frac{d\Sigma}{d\Omega}(q) = n_p \overline{f^2(q)} \cdot \overline{S}(q) \qquad\qquad (C.15)$$

where $\overline{S}(q)$ is the effective single component structure factor. In practice, $\overline{S}(q)$ is calculated using the monodisperse structure factor at the average sphere radius, but is strictly defined by appropriate matching with the exact multicomponent expression, Equation C.9. This approximation is superior to the decoupling approximation for hard sphere interactions and moderate polydispersity (<20%).

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