2018 NIST Center for Neutron Research Summer School
on Small Angle Neutron Scattering and Neutron Reflectometry

NGB30 SANS
Measuring depletion attraction in colloidal silica with SANS

Abstract

We will use small angle neutron scattering (SANS) to study the depletion attractions between colloidal silica particles introduced by adding low molecular weight polyethylene glycol (PEG) polymers to the solution. The measurement will illustrate the advantage of using contrast matching in neutron scattering as well as introduce data treatment and analysis. The physics behind the sample interactions as well as the design of the SANS experiment are introduced here. References are given for more in-depth information.

1. Introduction

Mixtures of colloidal particles and polymers are everywhere, from paints, toners and lubricants, to cosmetics, pharmaceuticals and processed foods and even soils and biological systems. In some cases, the polymer helps ***stabilize*** the particles by introducing a ***repulsive steric force*** between the particles. While in other cases, the polymer ***destabilizes*** the colloidal suspension and leads to particle aggregation by introducing an ***attractive depletion force***.

Figure 1 is pictures of a colloidal solution where adding polymer caused aggregation in an otherwise stable particle solution. The image on the left is a stable solution of particles that is optically transparent, while the image on the right is the exact same particles but with added polymer. The solution with added particles is cloudy and has phase separated, simply by adding a polymer to the mix.

Figure 1. (left) Image of a stable colloidal silica solution and (right) a two-phase solution that formed after adding PEG due to depletion interactions. Images are reproduced from Kumar et al.(1)

Whether adding polymer will stabilize or destabilize the particles will depend on the specific system, e.g. polymer chemistry, molecular weight, and concentration as well as particle size and surface chemistry. Understanding the structure and interactions in colloidal solutions is both a fundamentally interesting question but also practically important for the formulation of colloidal suspensions that we encounter in our everyday lives.

1.1.Depletion interactions in colloid-polymer mixtures

In this experiment we will study the effects of adding polyethylene glycol (PEG) of varying molecular weights to a colloidal silica solution. In these systems, adding PEG leads to *depletion attraction* between the particles and the particles aggregate and crash out of solution at high polymer concentrations.

How does adding a polymer lead to particle aggregation? Adding polymers, small molecules or small particles to a colloidal suspension that do not adsorb to the colloid's surface lead to an attractive interaction known as the depletion force. The basic concept behind depletion attraction is illustrated in Figure 2. When the distance between the particles is less than the polymer size, typically given by the polymer radius of gyration R_g, the polymer is excluded from the space between the particles. The region between particles where there is no polymer is known as the depletion zone. There is an osmotic pressure between depletion zone with no polymer and the surrounding solvent that contains the bulk polymer concentration, φ, that drives solvent *out* of the depletion zone and *into* the bulk solvent.(2) The driving of solvent from between the particles and into the bulk solvent is the depletion pressure that drives the particles together.

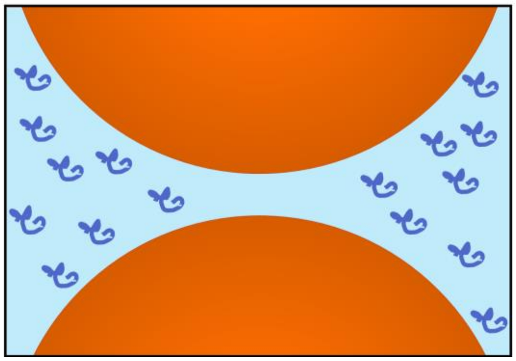

Figure 2. Cartoon illustration of depletion attraction between particles. Nonadsorbing polymers (purple coils) are excluded from the region between the particles (orange spheres) and produce an attraction with a range on the length scale of the polymer R_g. Image adapted from the book by Israelchvili.(2)

The depletion pressure between the particles is the same as the osmotic pressure, $P = -\varphi RT$ in which R is the ideal gas constant and T is temperature. Increasing the polymer concentration increases the osmotic pressure and therefore the depletion pressure that drives the particles together and leads to aggregation. It is important to note that this is only true when the separation between particles D is smaller than the polymer size given by their radius of gyration, R_g, *i.e.* when $D < R_g$. It is also important to keep in mind that the depletion forces are relatively short range and only act over a distance of $\approx R_g$. To get longer range attractions, we need polymers with a larger R_g which corresponds to a higher molecular weight.

1.2. SANS from colloidal solutions: measuring interactions between particles

The previous section suggested that adding PEG will introduce an attractive depletion interaction between the colloidal silica particles, but how do we measure this interaction? As you might have guessed being at a neutron scattering summer school – we can measure the interactions with small angle neutron scattering (SANS). But how does scattering from a colloidal solution tell us about the interactions?

The scattering from a monodisperse colloidal solution, the coherent scattering intensity $I(q)$ can be expressed as

$$I(q) = \phi V \Delta\rho^2 P(q) S(q) \qquad [1]$$

Where ϕ is the particle volume fraction, V is the particle volume, $\Delta\rho$ is the difference in scattering length density between the particles and the solvent, also called the scattering contrast, $P(q)$ is the form factor and $S(q)$ is the structure factor. In these expressions, q is the scattering vector and is given by $q = 4\pi/\lambda \sin\theta$ and 2θ is the scattering angle. The goal of an elastic scattering experiment is to measure the structure and interactions in the samples, and to do this, we need to determine the contrast, form factor and structure factor for our sample. We will discuss each of these terms in the next 3 sections.

1.2.1. Scattering contrast : $\Delta\rho^2$

To have enough scattered intensity to characterize the sample, there must be scattering contrast (Δρ) between the sample and the surrounding solvent. In other words, the sample must 'look' different from the solvent as far as the neutrons are concerned.

Neutrons interact with the nucleus of the of an atom and the probability that the neutron will interact with a given atomic nucleus is characterized by the so called scattering length, b_i. The scattering length varies by element and by isotopes for a given element, which is a unique advantage of neutron scattering. Scattering by X-rays will increase with the atomic number while the neutron scattering length varies seemingly randomly across the periodic table. The b_i values for the elements and their isotopes are tabulated and can be found on the NCNR website: https://www.ncnr.nist.gov/resources/n-lengths/

We are interested in length scales that are much larger than atomic distances in small angle scattering, so it is useful to define the scattering length density (SLD), ρ, of a material,

$$\rho = \sum_{i}^{N} \frac{b_i}{V} \qquad [2]$$

In which V is the volume containing N atoms. Calculating the SLD averages the scattering length over the volume of the material, and we are most interested in the differences in materials properties ρ_1 and ρ_2 where 1 and 2 are our particles and solvent for example. We refer to the difference in SLDs are the scattering contrast, $\Delta\rho = \rho_1 - \rho_2$. The larger the $\Delta\rho$ the larger the scattered intensity. The SLD's can be calculated by hand from the tabulated values of b_i or the NCNR has an online calculator: https://www.ncnr.nist.gov/resources/activation/

Shown in Table 1 are calculated values for the SLD of silica, PEO, D_2O and H_2O, the materials we will be using in our experiment. Notice that the ρ values for H_2O and D_2O differ by an order of magnitude and by sign. The difference is because hydrogen and deuterium have very different scattering lengths despite being isotopes (remember b_i varies with element *and* isotopes). This means that we can vary the H and D content in our samples to change the scattering contrast for different components. In fact, it is often possible to find conditions where we match the SLD of the solvent to one of the components of the sample, a technique referred to as contrast matching. Contrast matching is a unique advantage of neutron scattering compared to other scattering techniques and makes SANS a very powerful tool for studying multicomponent systems – such as the ones we are interested in studying in this experiment.

Material	**Chemical formula**	**Mass density (g/cm^3)**	**Scattering length density (cm^{-2})**
Silica	SiO^2	~ 2.2	~ 3.4 x 10^{10}
PEG	$(C_2H_4O)_n$	1.21	0.685 x 10^{10}
Heavy water	D_2O	1.1	6.34 x 10^{10}
Light water	H_2O	1	-0.561 x 10^{10}

Table 1. Calculated scattering length densities for the materials we will be using in our experiment. Note that the values for silica and PEG are based on densities from literature and may not be precise. In particular, the silica density can vary with particle preparation method.

We are interested in measuring how adding PEG affects the interactions between silica particles in solution, which means we will have 3 components in our system: silica, PEO and aqueous solvent (H_2O or D_2O). Comparing the values in Table 1 suggest that these three components all have different SLDs and if we prepared our samples in H_2O or D_2O, we would be able to see scattering from both the silica and PEG as depicted in left cartoon in Figure 3. However, we are most interested in looking at the interactions between the silica particles, so we can instead prepare samples in a mixture of H_2O/D_2O with the same SLD as the PEG (right cartoon in Figure 3). At this contrast condition, the PEG effectively 'disappears' and we will only see scattering from the silica particles which will greatly simplify our data analysis.

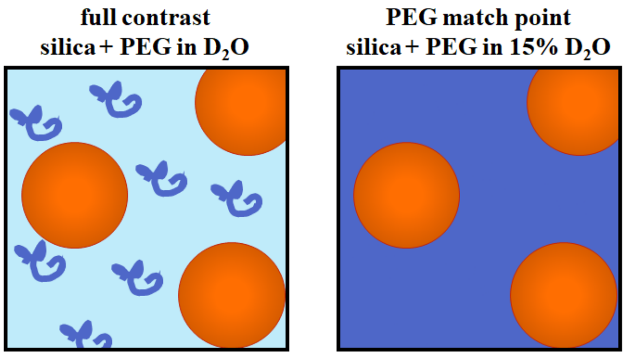

Figure 3. Cartoon illustration of the neutron contrast for silica (orange spheres) and PEG (purple coils) prepared in D_2O versus the PEG match point at 15% D_2O.

1.2.2. Form Factor: *P(q)*

The form factor is scattering from interference from different parts of the same object and therefore provides information on the structure of the scattering object. $P(q)$ is related to the Fourier transform of the real space density distribution and expressions for $P(q)$ for the scattering common shapes such as spheres, cylinders, and ellipsoids have been developed.

In this experiment, we will fit our data with a form factor model for spheres. The general expression for the form factor of a sphere is given by

$$P(q) = \left[\frac{3(\sin qR - qR\cos qR)}{(qR)^3}\right]^2 \qquad [3]$$

Where R is the sphere radius. This function will have zeros at $qR = 4.493.\ 7.725, \ldots \cong (2k + 1)\pi/2$, meaning there will be minima in the scattered intensity that directly correspond to the sphere radius.(3) Shown in Figure 4 is the calculated form factor for spheres with R = 8 nm, the same size particles we will be studying in our experiments.

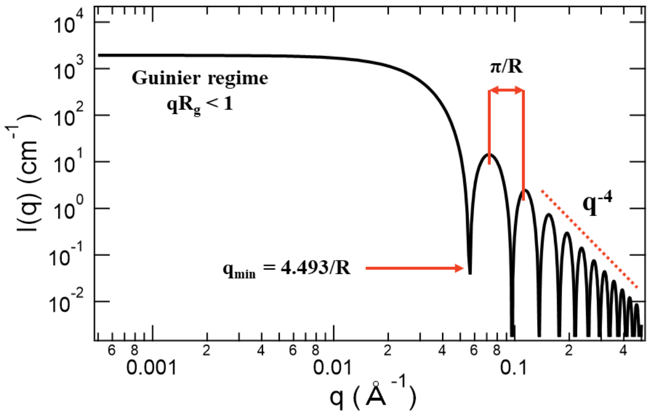

Figure 4. Calculated scattering for monodisperse, spherical silica particles with a radius of R = 8 nm.

1.2.3. Structure Factor: *S(q)*

The structure factor *S(q)* is due to interference from different objects in the sample. In a crystalline lattice, the structure factor describes the positions of different atoms in the lattice. In solution, *S(q)* is a measure of the correlation function between the center of masses of the different particles. Because the relative positions are determined by their interaction potential, *S(q)* therefore contains information on the *interactions* between objects in solution.

At low concentrations, there are no correlations between the particle positions and $S(q) \approx 1$. The scattering pattern from dilute solutions is therefore determined only by the form factor as $I(q) = AP(q)$. At higher concentrations, the interactions between the objects in solution need to be taken into consideration.

Because *S(q)* arises from interference *between different* objects, we see the effects at larger length scales which corresponds to the scattering at low q. In the limit of $q \rightarrow 0$, the scattered intensity is related to the osmotic compressibility of the system:

$$S(q \rightarrow 0) = k_B T \left(\frac{\partial n}{\partial \Pi}\right) \qquad [4]$$

Where n is the particle number density and is the Π osmotic pressure.(4) Therefore $S(q \rightarrow 0) > 1$ for attractive interactions when the system is more compressible and $S(q \rightarrow 0) < 1$ for repulsive interactions. Expressions for *S(q)* have been determined from statistical mechanical theories for the inter-particle potential. Details on how to calculate *S(q)* are beyond the scope of this write-up, but the calculated structure factors for sticky hard sphere attractive interaction as well as the repulsive hard sphere and Coulombic interactions are shown in Figure 5. As can be seen in the graph, *S(q)* increases at low q for the attractive interactions and is less than 1 for repulsive interactions.

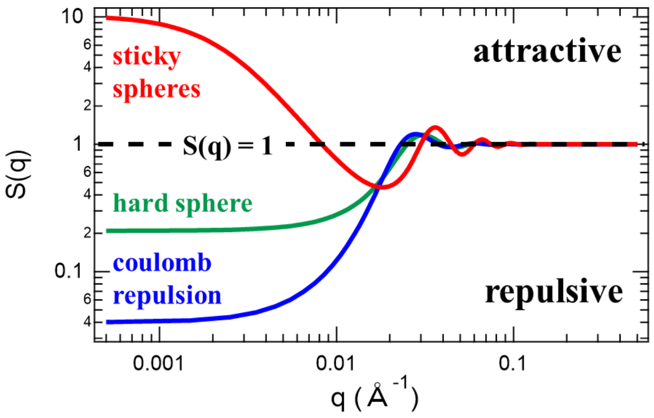

Figure 5. Calculated structure factors for sticky hard spheres (red), hard spheres (green), and charged spheres with Coulombic repulsion (blue). The calculations are for 100 nm spheres with 10% polydispersity.

2. Planning a SANS experiment

Now that we know what we are interested in measuring, how to we go about planning a successful experiment? To get good data we want to maximize the scattered intensity from our sample and minimize the background. We already introduced important things to consider for SANS sample preparation above such as making sure there is enough scattering contrast to get a good signal (Section 1.2.1) and if our samples are in a dilute limit where $S(q) \to 1$ (Section 1.2.3), but there are a few more things to think about both in terms of sample preparation and measurements before starting a SANS experiment that we discuss below.

2.1. Sample thickness

What sample thickness do we need for a SANS experiment? Choosing a sample path length not only determines the amount of sample needed for the experiment, but more importantly, the measured scattering intensity from the sample.

The intensity that we measure is proportional to the sample thickness, d_s, and sample transmission, T. Increasing d_s increases the measured intensity – but at the same time, decreases the sample transmission. This tradeoff means that there should be an optimum d_s to maximize the measured intensity.

To find the optimum d_s, we first need to consider how increasing the thickness affects the sample transmission. The sample transmission is the fraction of neutrons that pass through the sample without being scattered or absorbed and is given by:

$$T = e^{-\Sigma_t d_s} \qquad [5]$$

Where Σ_t is the total cross section and equal to the sum of the coherent, incoherent, and absorption macroscopic cross sections: $\Sigma_t = \Sigma_c + \Sigma_i + \Sigma_a$.

The absorption cross section (Σ_a) depends on the cross section of elements in the sample and can be calculated from tabulated values for the different elements if the mass density and chemical composition of the sample are known. Σ_a is wavelength dependent and increases linearly with λ for almost all wavelengths, meaning the sample transmission will also vary wavelength and must be measured for very wavelength used during the experiment (see Section 3). The incoherent cross section (Σ_i) can also be estimated from tabulated values for the different elements in the sample as well but will also depend on the atomic motions in the sample and therefore can vary slightly with temperature. Last but not least is the coherent cross section (Σ_c) which will depend on both the structure and dynamics of the material. (which should not be a surprise since Σ_c is what we are aiming to measure!)

After estimating the sample transmission, the optimum sample length can be calculated because the measured intensity is proportional to

$$I_{meas} \propto d_s e^{-\Sigma_t d_s} \tag{6}$$

Which will have a maximum at $d_s = 1/\Sigma_t$. The optimum transmission, $T_{opt} = 1/e \approx 0.37$. The sample thickness that gives T_{opt} for a given sample is known as the "1/e-length".

Estimating T for our samples is straightforward but can be time consuming. Fortunately, there are tools to help. The NCNR's Web-based Neutron activation and scattering calculator (https://www.ncnr.nist.gov/resources/activation/) not only computes the scattering length density, but also estimates the incoherent and absorption cross sections and the 1/e-length for the entered materials. It is good to estimate the optimum thickness before starting a SANS experiments. In some cases, we can increase the sample thickness to get better counting statistics in shorter times or in other cases, we may need to decrease the sample thickness to prevent multiple scattering discussed next Section 2.2.

2.2. Multiple scattering

It is possible to have *too* much scattering. Analyzing SANS data assumes that the neutron is only scattered *once* as it passes through the sample and that any measured scattering angle is therefore related to the structure of the sample. However, this assumption may not be true is samples that scatter very strongly, *i.e.* the neutron may scatter multiple times while passing through the sample. Multiple scattering distorts the shape of the measured SANS curves and makes data analysis almost impossible. (5)

If the sample scatters too strongly, we need to consider ways to reduce the scattered intensity such as decreasing the scattering contrast $\Delta\rho^2$ or reducing the sample thickness. A good check before an experiment is to estimate Σ_i and Σ_a, because if $\Sigma_c >> \Sigma_i + \Sigma_a$ the sample thickness should be reduced so that the transmission due to the coherent scattering remains higher than 0.9 rather than $T_{opt} = 0.37$ to avoid multiple scattering effects.

2.3. Choosing an instrument

Here at the NCNR we have a total of 5 SANS instruments: 3 SANS, very small angle scattering (VSANS) that is currently in commissioning and ultra-small angle neutron scattering (USANS). Each type of instrument is designed to cover a specific q-range as illustrated below in Figure 6. It is important that we know the length scales of interest the sample before picking an instrument. SANS is best suited for studying samples from ≈ 1 nm to ≈ 100 nm while USANS captures length scales from ≈ 100 nm to ≈ 20 μm. VSANS bridges these two extremes and allows us to measure samples with size scales ranging from ≈ 1 nm to ≈ 1 μm.

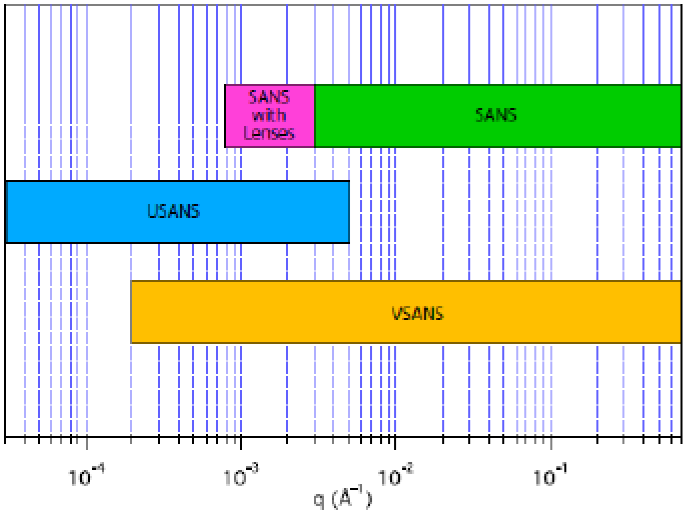

Figure 6. Comparison of the accessible q ranges for the BT-5 USANS instrument, NG-3 and NG-7 SANS instruments, and VSANS instrument in commissioning. The plot is reproduced from reference (6).

The silica particles that we will be studying have a radius R ≈ 8 nm, and the length scales of interest fall within the range we can study with SANS. We will be running on the NGB30 SANS instrument, but how do we select the q-range we want to measure? Figure 4 shows the form factor calculated for sphere with an 8 nm radius, and we see the feature corresponding to the particle radius at q > 0.04 Å^{-1}. We also know from Section 1.2.3 that we will see the effects of the structure factor at low *q*. Therefore, we will want to measure as wide of a *q*-range as possible to cover all the length scales of interest for these experiments. Though in other experiments, we may want to choose a different *q*-range to focus on a specific structural feature or watch a structure evolve with time or in response to a stimulus.

3. Running the Experiment

After all the planning, there are a few more things to take into consideration when we start our SANS experiment. We will need to run 'backgrounds' to subtract from our sample data. We also need to figure out how long to run the measurement to ensure that the data are not too noisy and that we have good statistic when it comes time to analyze the data. Each of these topics is discussed below.

3.1.'Backgrounds' to run

We are ultimately interested in the scattering from our sample, but there are additional measurements we need to make during a SANS experiment to correct for the "background." The neutrons counted by the detector come from 3 places: [a] neutrons scattered by the sample itself (and what we want to measure), [b] neutrons scattered by everything that is surrounding the sample as the beam passed through the sample, and [c] everything else such as stray neutrons that reach the detector without going through the sample and the electronic noise of the detector. To separate these contributions, we need to make 3 measurements during our SANS experiments:

1) Scattering from our *samples*, which will contain contributions from everything listed above (a, b and c), referred to as I_{sam} in the next section
2) Scattering from the *empty cell*, which includes scattering from everything around the sample but is not from the sample itself as well as the stray neutrons and detector sensitivity (b and c), referred to as I_{emp} in the next section
3) Counts measured with a neutron absorber in the sample position, which we call the blocked beam and will account for the stray neutrons that are measured as well as the detector sensitivity (c), referred to as I_{bgd}

We also need to measure the transmission of our samples as well as the empty sample cell to correctly subtract the background measurements listed above. Remember from Section 2.1 that transmission is wavelength dependent, so we may need to measure multiple transmissions depending on how we select our instrument configurations!

3.2. How long do we need to count?

Now that we know all the measurements we need to make to be able to correctly subtract the "background" from our data – how long we will need to measure?

A SANS experiment is an example of a counting experiment where the uncertainty in the measured intensity (the standard deviation, σ, to be exact) scales with the total number of counts I(t): $\sigma = \sqrt{I(t)}$. The longer we measure, the more total counts we accumulate and the lower the uncertainty. A good rule of thumb is to try to accumulate ≈ 500,000 from your sample *above the sample background* where the sample background may be the solvent or simply the empty cell. If the 500,000 are circularly averaged into 50 data points when plotting $I(q)$ vs. q, then we will have about 1000 counts per data point. This averaging would mean that the standard deviation on a given point is $\sqrt{1000} \approx 30,$ or about 3%, which is good enough in most cases. *It is important to remember that σ scale with $\sqrt{t}$, which means that if we needed to decrease our uncertainty by 2x (from 3% to 1.5%), then we would need to increase out counting time by a factor of 4.*

Along the same lines, how long should the background and empty cell be counted relative to the sample measurement? The $\sigma = \sqrt{I(t)}$ relationships means the optimum counting times are approximately

$$\frac{t_{background}}{t_{sample}} = \sqrt{\frac{background\ count\ rate}{sample\ count\ rate}} \qquad [7]$$

If the sample scattering is weak, then the background should be counted for as long as the sample (but not longer!). But if the sample scattering is strong, say 4x that of the background, then we would need to measure the background for half the time of the sample.

4. After the experiment

After we have completed our measurements, we will need to process the raw data to form that can be analyzed. In the next two sections we quickly review SANS data reduction and analysis.

4.1. Data reduction

What we mean by data reduction is to correct the measured scattering from the sample for the sources of background discussed in Section 3 as well as taking into consideration things such as the counting time and sample thickness to put the measured data on an absolute scale. The final data will be the scattering cross section per unit volume that we can analyze to answer the questions we set at the beginning of the experiment.

The background corrected intensity, I_{cor}, is calculated according to

$$I_{cor} = \left(I_{sam} - I_{bgd}\right) - \left(\frac{T_{sam+cell}}{T_{cell}}\right)\left(I_{emp} - I_{bgd}\right) \qquad [8]$$

And the corrected intensity is related to the differential cross section of our sample, $d\Sigma(Q)/d\Omega$ by

$$\left(\frac{d\Sigma(Q)}{d\Omega}\right)_{sam} = \frac{I_{cor}}{K\ d_s\ T_{sam+cell}} \qquad [9]$$

Where I_x denotes a measured scattering intensity, T_x a measured transmission, and d_s the sample thickness. We already talked about the different measured intensities and transmissions in Section 3. K is an instrumental scale factor that is specific to the instrument set up we use to measure our desired q range:

$$K = \varphi A \, \Delta\Omega \, \varepsilon \, \mathrm{t} \qquad [10]$$

Where:

φ = neutron flux at the sample (neutrons/cm^2/s)
A = area of incident beam on the sample
$\Delta\Omega$ = solid angle subtended by one pixel of the detector
ε = detector efficiency
t = counting time

Also note that the equation above is per pixel. The data reduction is performed on the 2D detector images, and the data are radially integrated to get $I(q)$ vs. q *after* the reduction.

At the NCNR we use macros written by Steve Kline in IGOR Pro to perform the data reduction.(7) Details on the reduction are reduction are provided in reference (7) and written documentation and video tutorials on the reduction software are also available on the NCNR's website: https://www.ncnr.nist.gov/programs/sans/data/red_anal.html

4.2. Data analysis

At this point, we have data on an absolute intensity that we can fit with models for the form factor and structure factor of our sample to determine how adding PEG affects the silica particle interactions. There are several software packages available to analyze small angle scattering data. We will be using SASView to model the data at the summer school. SASView is an analysis software package that is developed and managed by an international collaboration of scattering facilities. More information on SASView can be found here: https://www.sasview.org/.

5. Summary and Objectives

We have covered the basics of planning a SANS experiment, performing the measurements, reducing the data, and analyzing the data. During the summer school we will perform three series of measurements:

1) Measure a contrast variation series to determine the SLD of our silica particles
2) Determine the form factor of the silica spheres in the *dilute* limit where $S(q) \rightarrow 1$
3) Study the effects of PEG molecular weight on the depletion interactions by fitting a structure factor to the data

6. Links for helpful tools and resources

The SANS Toolbox, by Boualem Hammouda:
https://www.ncnr.nist.gov/staff/hammouda/the_SANS_toolbox.pdf

Table of scattering lengths:
https://www.ncnr.nist.gov/resources/n-lengths/

SLD Calculator:
https://www.ncnr.nist.gov/resources/activation/

Video documentation on the NCNR's data reduction by Steve Kline:
https://www.ncnr.nist.gov/programs/sans/data/movies/reduction_analysis_movies.html

SASView:
https://www.sasview.org/

7. References

1. Kumar S, Ray D, Aswal VK, & Kohlbrecher J (2014) Structure and interaction in the polymer-dependent reentrant phase behavior of a charged nanoparticle solution. *Physical Review E* 90(4):042316.
2. Israelachvili JN (2011) *Intermolecular and Surface Forces* (Elsevier) Third Ed.
3. Roe R-J (2000) *Methods of X-Ray and Neutron Scattering in Polymer Science* (Oxford University Press).
4. Chang J, *et al.* (1995) Structural and Thermodynamic Properties of Charged Silica Dispersions. *The Journal of Physical Chemistry* 99(43):15993-16001.
5. Schelten J & Schmatz W (1980) Multiple-scattering treatment for small-angle scattering problems. *Journal of Applied Crystallography* 13(4):385-390.
6. Liu Y, Yuan G, & Bleuel M (2014) *Gelation of spherical colloidal systems with bridging attractions*.
7. Kline S (2006) Reduction and analysis of SANS and USANS data using IGOR Pro. *Journal of Applied Crystallography* 39(6):895-900.