Small Angle Neutron Scattering Fundamentals

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Small angle neutron scattering (SANS) measurements are made at the NIST Center for Neutron Research in Gaithersburg, Maryland. Because NIST is a user facility, the data are nicely output by the experiment, but a 'black box' element exists as a result. I believe it is important to connect the fundamentals of neutron scattering with the data output by the user facility. While there are many useful sources to learn about SANS, I have tried to compile all of the most important information in this document. Most of this work is derived through the work of Squires, Pynn, and Hammouda [1, 2, 3]. An alternate version of this document can be found in my thesis, and I am grateful for the help of Boualem Hammouda and Claire McIlroy.

1 Scattering from a Single Nucleus

To understand how a real material scatters neutrons, the scattering from an individual nucleus must be addressed. Consider a nucleus at the origin that acts like a point-particle. Incident neutrons traveling with wavevector $\vec{k}_0 = (0, 0, k)$ and wavefunction $\psi = e^{ikz}$ spherically scatter off the nucleus with scattered wavevector $\vec{k'}$ and wavefunction

$$\psi_s = -\frac{b}{r} e^{i\vec{k'}\cdot\vec{r}}, \tag{1}$$

where $\vec{r}$ is the location of the observed wave with respect to the origin and b is the scattering length. The negative sign in Equation 1 is arbitrary but chosen so that $b > 0$ is repulsive. While the premise of scattering is a change in momentum ($\vec{k}_0 \neq \vec{k'}$), I will only discuss elastic scattering ($|\vec{k}_0| = |\vec{k'}| = k$). Additionally, I will only focus on isotropic scattering, so Equation 1 is rewritten as

$$\psi_s = -\frac{b}{r} e^{ikr}. \tag{2}$$

2 Scattering Length

As can be seen in Equation 2, b has units of length, though it defines the neutron-nucleus interaction. For x-ray scattering, $b \propto Z$ where Z is the atomic number; b is more complicated in neutron scattering. In general, b is a complex number where $\mathrm{Im}\, b$ is related to neutron absorption by a nucleus. Some elements like cadmium are strong absorbers of neutrons because $\mathrm{Im}\, b$ for these nuclei are significant. For most elements, particularly the elements found in proteins, $\mathrm{Re}(b) \gg \mathrm{Im}(b)$, so I consider $b = \mathrm{Re}(b)$ in the following sections.

Neutrons scatter from nuclei that have an apparent size defined by the differential cross section

$$\frac{d\sigma}{d\Omega} \equiv \frac{\text{Number of neutrons scattered per second into area } dS}{\Phi d\Omega} \tag{3}$$

where Φ is the incident flux and $d\Omega$ is a differential solid angle. With neutrons traveling at speed v, the number of neutrons scattered through a surface dS per second is

$$v dS |\psi_s|^2 = v dS \frac{b^2}{r^2} = v b^2 d\Omega, \tag{4}$$

and since the flux of incident neutrons

$$\Phi = v|\psi|^2 = v, \tag{5}$$

the differential cross section becomes

$$\frac{d\sigma}{d\Omega} = b^2. \tag{6}$$

Therefore, the total scattering cross section for a nucleus is

$$\sigma_{tot} = 4\pi b^2. \tag{7}$$

The nucleus appears, to the neutron, to be an object with total scattering cross section of σ_{tot}. σ_{tot} varies randomly with Z and even amongst isotopes [Figure 1]. b is a consequence of nuclear interactions and cannot be predicted by current theories of nuclear forces. Therefore, b must be measured experimentally for each isotope.

3 Origin of Coherent and Incoherent Scattering

In an assembly of N nuclei, where the i$^{\text{th}}$ nucleus is at position $\vec{R}_i$ with scattering length b_i, the incident wave with wavevector $\vec{k}_0$ is expressed as

$$\psi = e^{i\vec{k}_0 \cdot \vec{R}_i} \tag{8}$$

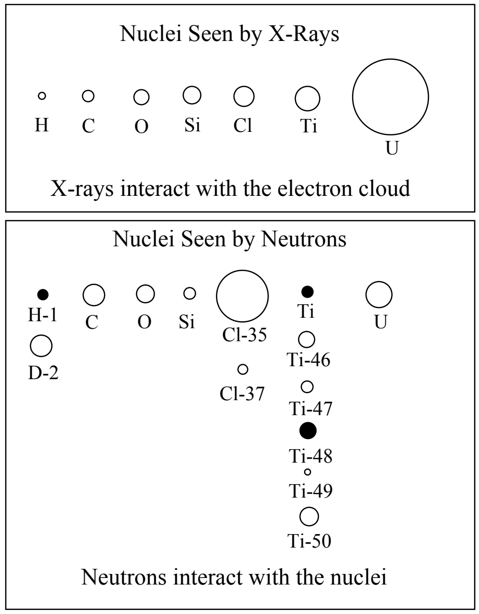

Figure 1: X-rays and neutron interactions with nuclei reprinted from Hammouda [3]. Solid symbols are for nuclei with negative scattering cross sections.

and the scattered wave with wavevector $\vec{k'}$ becomes

$$\psi_s(\vec{r}) = \sum_i^N e^{i\vec{k}_0\cdot\vec{R}_i}\left[\frac{-b_i}{|\vec{r}-\vec{R}_i|}e^{i\vec{k'}\cdot\left(\vec{r}-\vec{R}_i\right)}\right]. \tag{9}$$

Note that Equation 9 reduces to Equation 2 when $N = 1$ and $\vec{R}_i = (0, 0, 0)$.

Define the scattering vector $\vec{q}$ as the momentum transfer $\vec{q} = \vec{k}_0 - \vec{k'}$ and measure the wave at distances larger than inter-atomic distances ($\vec{r} \gg \vec{R}_i$). In the simplest scenario, all nuclei are identical with the same average scattering length $\bar{b}$. However, variations of nuclei positions or spin states with time cause fluctuations δb_i around $\bar{b}$ that are uncorrelated with fluctuations δb_j. Therefore, $b_i = \bar{b} + \delta b_i$. The total scattering cross section for an assembly of point particles, using Equations 3 & 9, becomes

$$\begin{aligned}\frac{d\sigma_{tot}}{d\Omega} &= \left\langle \bar{b}^2 \sum_i^N \sum_j^N e^{-i\vec{q}\cdot\left(\vec{R}_j-\vec{R}_i\right)} + N\left\langle \delta b^2\right\rangle\right\rangle \\ &= \frac{d\sigma_{coh}}{d\Omega}(\vec{q}) + \frac{d\sigma_{inc}}{d\Omega}\end{aligned} \tag{10}$$

where σ_{coh} and σ_{inc} are the coherent and incoherent scattering cross sections respectively. Coherent scattering depends on $\vec{q}$ and originates from scattering of different nuclei at the same time, creating an interference pattern from scattered waves. Incoherent scattering is caused by scattering from individual scatterers at different times that adds independently. As a result, the total scattering cross section

$$\sigma_{tot} = \sigma_{coh} + \sigma_{inc}. \tag{11}$$

For the remainder of this section, I will exclusively discuss σ_{coh} because only σ_{coh} contains structural information, and I rename $\sigma = \sigma_{coh}$ for convenience.

4 One Finite Sized Particle as an Assembly of Point Particles

Real objects can not always be considered point-particles. However, finite sized particles with volume V_P can be approximated by an arrangement of nuclei. Redefining $b_i = \bar{b}$, the coherent scattering cross section for an assembly of identical point particles becomes

$$\frac{d\sigma}{d\Omega}(\vec{q}) = \left\langle \left| \sum_i^N b_i e^{i\vec{q}\cdot\vec{R}_i} \right|^2 \right\rangle. \tag{12}$$

Extending the sum over nuclei into an integral over all space $\vec{r}$ inside of the particle, the scattering cross section becomes

$$\frac{d\sigma}{d\Omega}(\vec{q}) = \left\langle \left| \frac{1}{V_p} \int d\vec{r}\; b(\vec{r}) e^{i\vec{q}\cdot\vec{r}} \sum_i^N \delta(\vec{r} - \vec{R}_i) \right|^2 \right\rangle. \tag{13}$$

Instead of scattering from point nuclei at $\vec{r} = \vec{R}_i$, the scattering length density

$$\rho(\vec{r}) = \frac{b(\vec{r})}{V_p} \tag{14}$$

is defined. Additionally, the number density of scatterers

$$n(\vec{r}) = \sum_i^N \delta(\vec{r} - \vec{R}_i), \tag{15}$$

where $\langle n(\vec{r}) \rangle = n/V_P$, is equivalent to

$$n(\vec{r}) = \bar{n} + \Delta n(\vec{r}) \tag{16}$$

with a spatially fluctuating density $\Delta n(\vec{r})$ about an average density $\bar{n}$.

Equation 13 can then be rewritten as

$$\frac{d\sigma}{d\Omega}(\vec{q}) = \left\langle \left| \int d\vec{r} \rho(\vec{r}) e^{i\vec{q}\cdot\vec{r}} \left(\bar{n} + \Delta n(\vec{r})\right) \right|^2 \right\rangle . \tag{17}$$

Approximating $\rho(\vec{r}) = \rho$ inside the particle and separating the terms in the integral gives

$$\frac{d\sigma}{d\Omega}(\vec{q}) = \left\langle \left| \bar{n}\rho \int d\vec{r} e^{i\vec{q}\cdot\vec{r}} + \rho \int d\vec{r} e^{i\vec{q}\cdot\vec{r}} \Delta n(\vec{r}) \right|^2 \right\rangle . \tag{18}$$

The first integral only contributes when $q = 0$ and is not measured in a scattering experiment. The second integral is the Fourier transform of the density fluctuations in real space. Therefore, Equation 18 becomes

$$\frac{d\sigma}{d\Omega}(\vec{q}) = \left\langle \left| \rho \Delta V_P n(\vec{q}) \right|^2 \right\rangle . \tag{19}$$

Note that the scattering cross section only depends on ρ, V_P, and the density fluctuations in momentum space.

5 Origin of Contrast Factor

In the case of a general two-phase system where the i$^{\text{th}}$ component has volume V_i (total volume $V = V_1 + V_2$), scattering length density ρ_i, and density fluctuations $\Delta n_i(\vec{q})$, the $\vec{q} \neq 0$ scattering in Equation 18 is rewritten as

$$\frac{d\sigma}{d\Omega}(\vec{q}) = \left\langle \left| \rho_1 \int_1 \Delta n_1(\vec{r}) e^{i\vec{q}\cdot\vec{r}_1} + \rho_2 \int_2 \Delta n_2(\vec{r}) e^{i\vec{q}\cdot\vec{r}_2} \right|^2 \right\rangle , \tag{20}$$

where $\int_i$ is the integral over all of V_i. Given that $\Delta n_i(\vec{r}) = \Delta n_i(-\vec{r})$ and that the incompressibility assumption requires $\Delta n_1(\vec{r}) = -\Delta n_2(\vec{r})$,

$$\frac{d\sigma}{d\Omega}(\vec{q}) = (\Delta\rho)^2 V_1^2 \left\langle \Delta n_1(\vec{q}) \Delta n_1(\vec{q}) \right\rangle . \tag{21}$$

The contrast factor $\Delta\rho = (\rho_1 - \rho_2)$ in Equation 21 is an extremely important and powerful feature of SANS; a careful choice of $\Delta\rho$ greatly simplifies data interpretation.

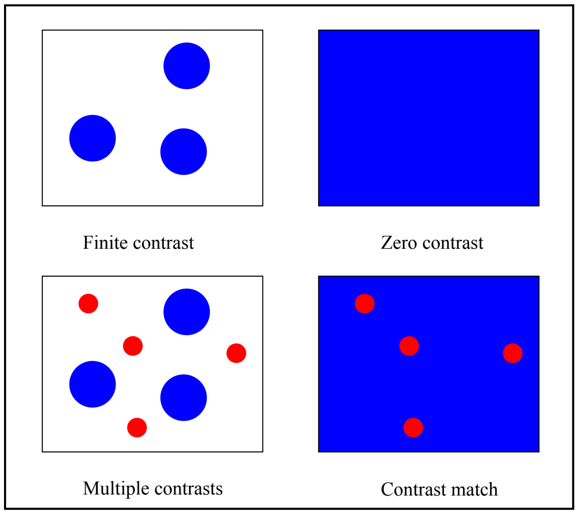

Figure 2: Changes in solvent scattering length density change contrast reprinted from Hammouda [3].

5.1 Contrast Matching

One of the advantages of neutron scattering is the ability to adjust the contrast factor $\Delta\rho$ between the scatterers and the solvent. Since $d\sigma/d\Omega(\vec{q}) \propto \Delta\rho^2$, the intensity of scattering is maximized by adjusting the solvent. Solvent adjustments are most frequently accomplished by isotope changes, since isotope changes dramatically affect the scattering length of the nucleus [Figure 1]. In aqueous solvents, some percentage of the water (H_2O) is replaced by deuterium oxide (D_2O) to maximize $\Delta\rho^2$.

Alternatively, the solvent can also be adjusted to selectively scatter from a particular part of the system instead of maximizing $\Delta\rho^2$. The most straightforward contrast variation involves mixing H_2O and D_2O to create a binary solvent with a desired average scattering length density ρ_{mix}. As schematized in Figure 2, a system with constituents A and B with ρ_{A} and ρ_{B} will scatter from both A and B. However, scattering will come from only A if $\rho_{\text{mix}} = \rho_{\text{B}}$.

6 Assembly of Finite Sized Particles

I have shown for the previous scenarios that $d\sigma/d\Omega(\vec{q}) = \langle |f(\vec{q})|^2 \rangle$, where $f(\vec{q})$ is a scattering amplitude. In the case of a point particle at $\vec{R}_i$, $f(\vec{q}) = -be^{i\vec{q}\cdot\vec{R}_i}$, whereas $f(\vec{q}) = \Delta\rho V_P \Delta n(\vec{q}) e^{i\vec{q}\cdot\vec{u}_i}$ for a finite sized particle centered at $\vec{u}_i$. Therefore, the scattering cross section for an assembly of N identical finite sized particles is

$$\frac{d\sigma}{d\Omega}(\vec{q}) = \left\langle \left| \sum_i^N \Delta\rho V_P \Delta n(\vec{q}) e^{i\vec{q}\cdot\vec{u}_i} \right|^2 \right\rangle. \tag{22}$$

Expanding this out, I get

$$\begin{aligned} \frac{d\sigma}{d\Omega}(\vec{q}) &= (\Delta\rho)^2 V_P^2 \left\langle \sum_i^N \sum_j^N \Delta n(\vec{q}) \Delta n(\vec{q}) e^{i\vec{q}\cdot(\vec{u}_i - \vec{u}_j)} \right\rangle \\ &= N(\Delta\rho)^2 V_P^2 \left\langle \Delta n(\vec{q}) \Delta n(\vec{q}) \right\rangle \left(1 + \frac{1}{N} \left\langle \sum_i^N \sum_{j\neq i}^N e^{i\vec{q}\cdot(\vec{u}_i - \vec{u}_j)} \right\rangle \right). \end{aligned} \tag{23}$$

Defining the single particle form factor

$$P(\vec{q}) \equiv \left\langle \Delta n(\vec{q}) \Delta n(\vec{q}) \right\rangle \tag{24}$$

and the structure factor

$$S(\vec{q}) \equiv \left(1 + \frac{1}{N} \left\langle \sum_i^N \sum_{j\neq i}^N e^{i\vec{q}\cdot(\vec{u}_i - \vec{u}_j)} \right\rangle \right), \tag{25}$$

Equation 23 becomes

$$\frac{d\sigma}{d\Omega}(\vec{q}) = N(\Delta\rho)^2 V_P^2 P(\vec{q}) S(\vec{q}). \tag{26}$$

7 Macroscopic Scattering Cross Section

The macroscopic scattering cross section is defined as

$$\frac{d\Sigma}{d\Omega}(\vec{q}) \equiv \frac{1}{V} \frac{d\sigma}{d\Omega}(\vec{q}), \tag{27}$$

where V is the volume of the sample; $d\Sigma/d\Omega(\vec{q})$ is an intensive property of the sample. Because of instrumental conditions, the actual measured scattering of the sample varies. However, the absolute scattering intensity $I(\vec{q})$ is calculated knowing the experimental parameters:

$$I(\vec{q}) = \left[\phi A \ell T \Delta\Omega \varepsilon t\right] \frac{d\Sigma}{d\Omega}(\vec{q}) \tag{28}$$

where ϕ is the neutron flux, A is the area of the sample, ℓ is the pathlength of the sample, T is the sample transmittance, $\Delta\Omega$ is pixel size in units of solid angle, ε is the efficiency of the detector, and t is the counting time for the experiment. With $I(\vec{q})$ known, a quantitative comparison can be made between measurements.

8 Scattering in Experiments

In a SANS experiment, a monochromatic neutron beam is directed through a collimated aperture and incident upon the sample. The sample scatters the neutrons over some angle onto a 2-dimensional detector as schematized in Figure 3; in the case of isotropic scattering, the detector is azimuthally averaged to determine $I(q)$. The scattering vector q is calculated by

$$q = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right), \tag{29}$$

where λ and θ are the neutron wavelength and scattering angle respectively.

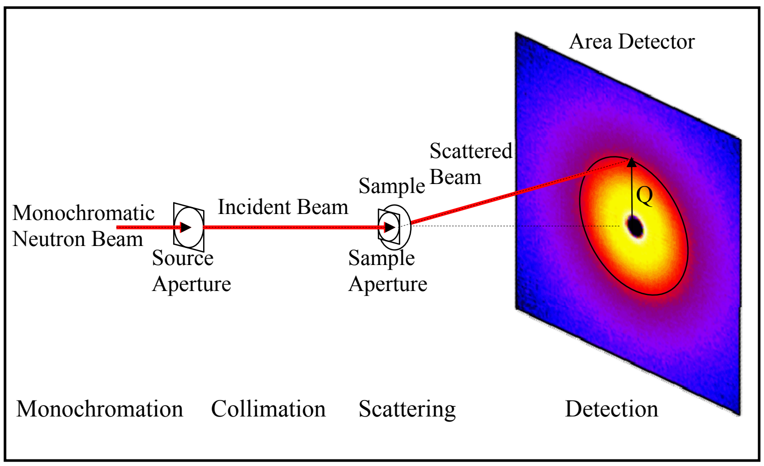

Figure 3: Schematic of SANS setup: monochromatic neutrons are focused onto a sample and scatter onto a 2-D detector reprinted from Hammouda [3]. If scattering is isotropic, 2-D scattering can be averaged onto a single curve.

9 Data Analysis

Once $I(q)$ is determined, data analysis begins. There are many different ways to analyze SANS data, but most of these methods require some *a priori* structural information or assumptions. However, the Guinier and Porod analyses techniques are the most basic because they require minimal assumptions. In the following subsections, I go through the derivations of each method.

9.1 Guinier Analysis

One of the simplest analysis types is an expansion of $P(\vec{q})$ using Equations 18 & 24. Define $\vec{s} = \vec{r} - \vec{r'} = (s_x, s_y, s_z)$, and set $\vec{r'}$ at the origin. The integrals can then be replaced by $\int d\vec{s}$: the distribution of distances $\vec{s}$. For small $\vec{q} \cdot \vec{s}$

$$P(\vec{q}) \approx \int d\vec{s} + i \int d\vec{s}\, (\vec{q} \cdot \vec{s}) - \frac{1}{2} \int d\vec{s}\, (\vec{q} \cdot \vec{s})^2 \tag{30}$$

where $\int d\vec{s}\, (\vec{q} \cdot \vec{s}) = 0$ from symmetry.

The quadratic term is expanded

$$\begin{aligned} \int d\vec{s} (\vec{q} \cdot \vec{s})^2 &= \int d\vec{s} (q_x s_x + q_y s_y + q_z s_z)^2 \\ &= \int d\vec{s} (q_x^2 s_x^2 + q_y^2 s_y^2 + q_z^2 s_z^2) \end{aligned} \tag{31}$$

from the same symmetry argument above. Because $(q_x^2 s_x^2 + q_y^2 s_y^2 + q_z^2 s_z^2) = q^2 s^2/3$, I can rewrite

$$\begin{aligned} F(\vec{q}) &\approx \int d\vec{s} - \frac{\frac{1}{6} \int d\vec{s}\, (q^2 s^2) \int d\vec{s'}}{\int d\vec{s''}} \\ &= V_0 \left(1 - \frac{q^2 R_G^2}{3} \right) \\ &\approx V_0 e^{-q^2 R_G^2/3} \end{aligned} \tag{32}$$

to order $\mathcal{O}(qR_G)^2$ where

$$R_G = \frac{1}{2} \frac{\int d\vec{s}\; s^2}{\int d\vec{s}}. \tag{33}$$

9.2 Porod Analysis

In the case of isotropic scattering, the scattering function can be rewritten in terms of the pair correlation function $g(s)$ as

$$I(q) \propto \int d\vec{s}\, \frac{sin(qs)}{qs}\; g(s), \tag{34}$$

where

$$\left\langle e^{-i\vec{q}\cdot\vec{s}} \right\rangle = \frac{sin(qs)}{qs} \tag{35}$$

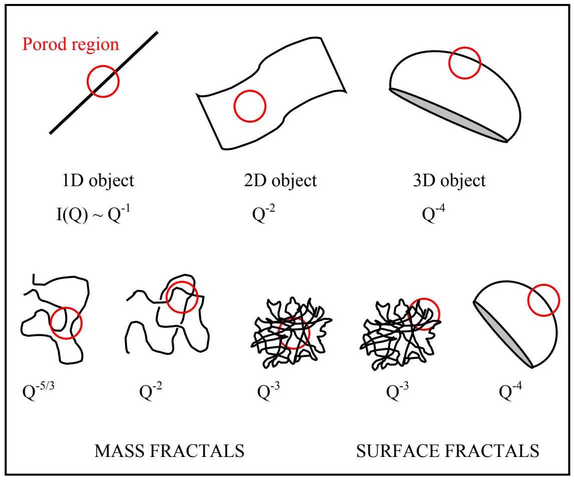

Figure 4: Structures associated with particular Porod slopes reprinted from Hammouda [3].

is the Debye approximation [4]. In a mass fractal, mass scales with s^D, where D is the mass fractal dimension. As a result, the pair correlation function $g(s) \propto s^{D-3}$ [5]. Using Equation 34,

$$I(q) \propto \frac{1}{q^D} \tag{36}$$

for the scattering of a mass fractal. D ranges between 0 and 3.

Systems that have surface fractals with dimension D_s have mass that scales with s^{2-D_s}, resulting in $g(s) \propto s^{3-D_s}$ [6]. Therefore,

$$I(q) \propto \frac{1}{q^{6-D_s}} \tag{37}$$

for the scattering of a surface fractal. Values of D_s range between 3 for a rough surface and 2 for a smooth surface. Note that $D_s = 2$ recovers the Porod scaling of $I(q) \propto 1/q^4$. Therefore, a microscopic picture of the structure inside a material can be determined by measuring the fractal dimension [Figure 4].

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