

Small-Angle Scattering Summary Equations*

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1 For the impatient ...

Guinier fit: radius of gyration

equation: $\log(I) = g_0 + g_1 \cdot Q^2$

obtain: $R_G = \sqrt{-3g_1}$

units: R_G : $1/Q$ units

Porod fit: specific surface area of scatterers

equation: $I(Q) = p_0 \cdot Q^{-p_1} + I_{bkg}$

obtain: $S_v = 0.159 \times 10^{12} p_0 / |\Delta\rho|^2$

units: Q : \AA^{-1}

I : cm^{-1}

S_v : cm^{-1}

p_0 : $\text{cm}^{-1} \cdot \text{\AA}^{-4}$

$|\Delta\rho|^2$: 10^{20} cm^{-4} (or 10^{28} m^{-4})

obtain: $S_m = 0.159 \times 10^8 p_0 / |\Delta\rho|^2 / \rho_m$

units: S_m : $\text{m}^2 \cdot \text{g}^{-1}$

ρ_m : $\text{g} \cdot \text{cm}^{-3}$

2 Introduction

A brief¹ summary of equations useful for basic analysis of small-angle scattering is presented. The magnitude of

the reciprocal-space scattering vector²,

$$|\vec{Q}| = Q = (4\pi/\lambda) \sin \theta \quad (1)$$

where 2θ is the scattering angle³. For a given Q , the strongest contribution to the observed scattering is likely due to objects of length scale $2\pi/Q$.

The intensity measured in the experiment, $I(Q)$, is proportional to the absolute intensity, expressed as differential cross-section per unit sample volume per unit solid-angle ($d\Sigma/d\Omega(Q)$),

$$I(Q) = I_0 \Omega t T_s \frac{d\Sigma}{d\Omega}(Q), \quad (2)$$

where I_0 is the apparent source intensity, Ω is the solid angle subtended by the detector from the sample, t is the sample thickness, and T_s is the sample transmission. The scattering is assumed to be coherent and also assumed such that either a single scattering event occurs within the sample or none occurs. Simplifications of Eq. 3 (below) exist for two limiting cases of scattering vector (low and high Q SAS regimes). It is necessary to define first some terms and we shall start with the intensity of small-angle scattering.

3 Scattered Intensity

$d\Sigma/d\Omega(Q)$ is an intensive property; it is not dependent on the physical dimensions or amount of the sample. It is described^{1-5,8} as the Fourier transform of the local scattering length density distribution, $\rho(\vec{r})$, where \vec{r} is a position vector within the sample,

$$\frac{d\Sigma}{d\Omega}(\vec{Q}) = V_s^{-1} \left| \int_{V_s} \rho(\vec{r}) e^{-i\vec{Q} \cdot \vec{r}} d^3\vec{r} \right|^2, \quad (3)$$

and the integral is over the sample volume, V_s . If $\rho(\vec{r})$ is constant over all \vec{r} , then $d\Sigma/d\Omega$ will be zero, thus only

²A variety of variables are used, depending on the text, synonymous with Q , such as h (used by Guinier and others) or k . Often $s = Q/2\pi$ is used.

³Some texts define the scattering angle as θ and thus Eq. 1 becomes $Q = (4\pi/\lambda) \sin(\theta/2)$. One must be careful to determine which definition is in use for a given presentation.

*<http://www.jemian.org/sasequations.pdf>

¹Also see <http://www.jemian.org/pjthesis.pdf>.

in the changes of the scattering length density, $\Delta\rho(\vec{r})$, between a scatterer and its surroundings are involved. For scattering from finely-divided solids, the scattering can be interpreted in terms of a particle size distribution. Lord Rayleigh^{6,7} has described the scattering from a single homogeneous particle of radius r and volume $V_p(r)$ as

$$\frac{d\Sigma}{d\Omega}(Q, r) = V_s^{-1} |\Delta\rho(r)|^2 |V_p(r) F_p(Q, r)|^2 \quad (4)$$

where V_s is the volume of the sample, $|\Delta\rho(r)|^2$ is the squared difference in scattering length densities between the scatterer of radius r and its average surroundings, $V_p(r)$ is the volume of a scatterer of radius r , and $F_p(Q, r)$ is a dimensionless form factor for the particle that describes the amplitude of scattering from a particle of a specific morphology (shape and orientation). The form factor is

$$F_p(Q, r) = F_p(\vec{Q}, \vec{r}) = V_p^{-1} \int_{V_p} e^{-i\vec{Q}\cdot\vec{r}} d^3\vec{r}. \quad (5)$$

4 Guinier Fit: $Q \cdot r \leq \sim 1.5$

The Guinier region³ for identical, randomly-oriented, non-interacting particles, applies for $Q \cdot r \leq \sim 1.5$.⁴ In this regime, Guinier has approximated Eq. 3 by

$$\lim_{Q \rightarrow 0} \frac{d\Sigma}{d\Omega}(Q) = N_v |\Delta\rho|^2 V_p^2 \exp\left[-\frac{1}{3}(QR_G)^2\right]. \quad (6)$$

N_v is the number of particles per unit volume, $V_p(r)$ is the particle volume, and R_G is the radius of gyration of the scatterer.

Rearranging terms, one fits data to the Guinier approximation by charting $\log(I)$ vs. Q^2 and fitting a straight line,

$$\log(I) = g_0 + g_1 \cdot Q^2, \quad (7)$$

where the constant term (g_0) is proportional to the concentration of scatterers (for constant size of scatterers) and the slope (g_1) reveals the radius of gyration:

$$R_G = \sqrt{-3g_1}, \quad (8)$$

and is in $1/Q$ units (typically Å or nm).

Strictly speaking, the Guinier relation holds for $Q_{MAX} \cdot R_G \leq 1.2$ where R_G is the radius of gyration determined from the slope of a $\log(I)$ vs. Q^2 fit for scatterers of any arbitrary shape and Q_{MAX} is the largest Q value included in the determination of R_G . (If the scatterers are spherical, then this constraint can be relaxed to $Q \cdot R_G \leq 1.8$.) Note that Eq. 6 is derived from a Taylor-series expansion in Q of Eq. 2, dropping odd-order terms.

If there is noticeable curvature in the chart of $\log(I)$ vs. Q^2 , then clearly, Eq. 6 will not apply.

If SAS data are on an absolute scale (of $\frac{d\Sigma}{d\Omega}(Q)$), then it may be possible to derive the concentration of scatterers. For spherical scatterers, the radius of scatterer is

$$R_S = \sqrt{\frac{5}{3}} \cdot R_G. \quad (9)$$

Thus, the scatterer volume

$$V_p = \frac{4}{3}\pi r^3. \quad (10)$$

and the concentration of scatterers (N_v is the number of scatterers per unit sample volume) is

$$N_v = \frac{\exp(g_0)}{|\Delta\rho|^2 V_p^2}. \quad (11)$$

When $I(Q)$ (and thus e^{g_0}) is expressed in cm^{-1} , $|\Delta\rho|^2$ in 10^{20} cm^{-4} (or 10^{28} m^{-4}), and V_p in Å^3 , then

$$N_v = 10^{28} \cdot \frac{\exp(g_0)}{|\Delta\rho|^2 V_p^2}. \quad (12)$$

Expressed in terms of R_G (in Å^{-1}) for known spherical scatterers,

$$N_v = 1.231 \times 10^{26} \cdot \frac{\exp(g_0)}{|\Delta\rho|^2 R_G^6}. \quad (13)$$

5 Porod Fit: $Q \cdot r \gg 1$

The other limiting case is the Porod region, in the tail of the SAS curve, for $Q \cdot r > 10$. The Porod region provides information about the average surface area per unit volume of sample, S_v , where the average is weighted towards the smaller particles if there is a distribution of sizes.

$$\lim_{Q \rightarrow \infty} \frac{d\Sigma}{d\Omega}(Q) = 2\pi S_v |\Delta\rho|^2 Q^{-4}. \quad (14)$$

S_v is the total scattering surface area per unit volume of sample irradiated by the beam and is determined from the slope of a plot of $\log(d\Sigma/d\Omega)$ versus $\log(Q)$ or from the intercept of a plot of $Q^4 d\Sigma/d\Omega$ vs. Q^4 . The slope of the latter plot is often interpreted as the experimental background. In cameras with perfect collimation (*i.e.*, pinhole geometry), the scattering is proportional to Q^{-4} whereas for slit-collimation cameras, the scattering is proportional to Q^{-3} .

There are (at least) two ways of fitting a Porod line to SAS data. In either case, one should be careful about the

contribution of a flat background, I_{bkg} , to the determination of the fit. Generally, fit $I(Q)$ vs. Q according to

$$I(Q) = p_0 \cdot Q^{-p_1} + I_{bkg}. \quad (15)$$

The exponent p_1 should be very close to 4⁴ or the validity in using Eq. 14 to determine S_v is compromised. More simply, one charts $I(Q)$ vs. Q and fits a straight line

$$I(Q) = p_0 \cdot Q^{-p_1}. \quad (16)$$

Again, $p_1 \sim 4$ must be assured. However, presence of I_{bkg} can complicate use of Eq. 16.

Specific surface area of scatterers (S_v , the total surface area of scatterers per unit volume of sample) can be determined from p_0 if the data are on an absolute scale,

$$S_v = \frac{p_0}{2\pi |\Delta\rho|^2}. \quad (17)$$

When, as above, $I(Q)$ is in units of cm^{-1} , Q in \AA^{-1} , and $|\Delta\rho|^2$ in 10^{20} cm^{-4} (or 10^{28} m^{-4}), then (noting $1/2\pi \simeq 0.159$)

$$S_v = 0.159 \times 10^{12} \frac{p_0}{|\Delta\rho|^2}. \quad (18)$$

Often, S_m (the total surface area of scatterers per unit mass of sample) is desired (where $S_m = S_v/\rho_m$):

$$S_m = 0.159 \times 10^8 \frac{p_0}{|\Delta\rho|^2 \rho_m}. \quad (19)$$

and ρ_m is the mass density of the sample in $\text{g}\cdot\text{cm}^{-3}$.

6 Scattering length density and contrast

When absolute intensities are available, one can use the previous equations to be quantitative about the amount or concentration of scatterers present. To harvest this additional information, it is necessary to describe the composition of the scatterers and their average surroundings. If intensities are on an arbitrary scale, then calculations of scattering length density and contrast are not generally useful.

The *scattering length density* is the total scattering length b of a substance per unit volume V and is calculated from the composition of the substance. In general, the density of the scattering entity,

$$\rho = \sum_i c_i b_i \quad (20)$$

⁴For slit-smeared intensity, $I = I_0 Q^{-3} + I_{bkg}$ thus p_1 should be very close to 3.

where c_i is the concentration (per unit volume) and scattering length, b_i , of component i in the sample, respectively, and the sum is over all components.

From Eq. 4, the intensity of SAS is proportional to the squared difference between the scattering length density of a scatterer, ρ_s , and that of average surroundings, ρ_m . This term, $|\Delta\rho|^2 = |\rho_s - \rho_m|^2$, is called the *scattering contrast*⁵. Thus,

$$|\Delta\rho|^2 = \left| \sum_i \Delta c_i b_i \right|^2, \quad (21)$$

where Δc_i is the difference in concentration of component i between the scatterer and its average surroundings.

In the case of neutrons, one consults tables of b_i , which are different for each isotope.⁴ The X-ray scattering length density, ρ_{e^-} , (where the subscript e^- signifies the *effective* density of electrons) requires further explanation. For X-ray energies near an electron binding energy, this effective density will decrease. This variation is described by

$$f = f_0 + f'_Z(E) + i f''_Z(E), \quad (22)$$

where $f_0 \sim Z$ in the small-angle regime, Z is the atomic number, and $f'(E)$ and $f''(E)$ are the energy-dependent corrections⁶ to the atomic scattering factor. Consequently, b_i is the effective scattering length of the electrons. On average, the scattering length of a single electron is its classical (Thomson) radius,

$$r_{e^-} = \frac{e^2}{4\pi\epsilon_0 m c^2}, \quad (23)$$

which is approximately 2.818 fm. The total effective scattering length of electrons in a given atom is given as

$$b = (r_{e^-})f. \quad (24)$$

By summation over all of the atoms in the sample, where Z is the atomic number,

$$\rho_{e^-} = (r_{e^-}) \sum_Z c_Z f_Z. \quad (25)$$

Thus, Eq. 21 for X-rays:

$$|\Delta\rho_{e^-}|^2 = \left| (r_{e^-}) \sum_Z \Delta c_Z [Z + f'_Z(E) + i f''_Z(E)] \right|^2. \quad (26)$$

Due to the complex nature of the atomic scattering factor, f_Z , the scattering length density for X-rays, ρ_{e^-} , is also a complex number. The same argument may also be

⁵Some texts define the scattering contrast as the difference between scattering lengths, $\Delta\rho = \rho_s - \rho_m$. Again, one must be careful which definition is in use.

⁶also known as anomalous dispersion corrections

made in the case of neutrons where b_i is complex for some isotopes.

Often, SANS (neutron) scattering length densities are expressed in terms of cm/cm^3 , or more simply cm^{-2} . Typical dimensions are of order 10^{10} - 10^{11} cm^{-2} . For the scattering contrast ($|\Delta\rho_{e^-}|^2$), typical values are in the range of 10^{20} - 10^{22} cm^{-4} . (Another common unit for expressing cross-section in neutron scattering is the *barn* where $1 \text{ barn} = 10^{-24} \text{ cm}^{-2}$ but this is not commonly used in SANS.)

In X-ray scattering (SAXS), the electron is principally responsible for the scattering. Again, scattering length densities are often represented in terms of cm^{-1} with typical values of order 10^{10} - 10^{11} cm^{-2} (note similarity to SANS). Thus, typical contrasts are in the range of 10^{20} - 10^{22} cm^{-4} .

When SI units are desired or required, the most common unit (consistent with the preceding paragraphs) expressed contrast in the range of 10^{28} - 10^{30} m^{-4} .

Another set of units also used in SAXS are $\text{e}^- \cdot \text{\AA}^{-3}$ and these are easy to express and typeset since they often do not require massive powers of ten. This set of units tells home many *effective* electrons are scattering in a given volume of sample. Using the classical electron radius (Eq. 23) to compute the cross-sectional area of an electron ($2\pi r_{e^-}^2$), one can convert to $\text{cm}^{-4} = 4.990 \times 10^{23} \text{ e}^- \cdot \text{\AA}^{-3}$ (or for SI: $\text{m}^{-4} = 4.990 \times 10^{31} \text{ e}^- \cdot \text{\AA}^{-3}$).

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