4. Scattering techniques

The determination of molecular organisation within colloidal systems is an important aspect when studying relationships between physical properties and molecular structure. Scattering techniques provide the most obvious methods for obtaining quantitative information on size, shape and structure of colloidal particles, since they are based on interactions between incident radiations (e.g., light, X-ray or neutrons) and particles. The size range of micelles, microemulsions, or other colloidal dispersions is approximately 10 – 10^4 Å, so valuable information can be obtained if the incident wavelength, λ , falls within this range. Therefore, microemulsion droplets or micelles, in the order of 10^2 Å in size, are well characterized by X-ray ($\lambda = 0.5 - 2.3$ Å) and neutrons ($\lambda = 0.1 - 30$ Å), while for larger colloidal particles, light scattering (λ = 4000 – 8000 Å), is best. In addition, considering the Bragg equation that defines the angle of diffraction θ of radiation of wavelength λ for a separation of lattice planes d:

$$\lambda = 2d\sin\theta \tag{4.1}$$

it can be seen that nanometre-sized particles such as microemulsion droplets will scatter at small angles, so that small-angle neutron scattering (SANS) can be used to study such systems [1].

Although the first neutron reactors were built in the late 1940's and 1950's, literature for application of neutron scattering to condensed matter appeared only in the late 1970's. In the last twenty years, with the development of more powerful neutron production sites, and progress in the technology of large area detectors and high resolution spectrometers, SANS has become a more accessible technique and, in particular, has been used successfully to study micellisation, microemulsion and liquid crystal structures. SANS is thus a relatively recent technique but is now one of the most powerful tools to characterize molecular aggregates.

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In the following sections a summary of neutron scattering theory and methods for SANS data analysis is given.

4.1 GENERAL BACKGROUND

4.1.1 Neutrons

A neutron is an uncharged (electrically neutral) subatomic particle with mass m = 1.675×10^{-27} kg (1,839 times that of the electron), spin $\frac{1}{2}$, and magnetic moment -1.913 nuclear magnetons. Neutrons are stable when bound in an atomic nucleus, whilst having a mean lifetime of approximately 1000 seconds as a free particle. The neutron and the proton form nearly the entire mass of atomic nuclei, so they are both called nucleons. Neutrons are classified according to their wavelength and energy as "epithermal" for short wavelengths ($\lambda \sim 0.1$ Å), "thermal", and "cold" for long wavelengths ($\lambda \sim 10$ Å). The desired range of λ is obtained by moderation of the neutrons during their production, either in reactors or spallation sources.

Neutrons interact with matter through strong, weak, electromagnetic and gravitational interactions. However, it is their interactions via two of these forces – the short-range strong nuclear force and their magnitude moments – that make neutron scattering such a unique probe for condensed-matter research. The most important advantages of neutrons over other forms of radiation in the study of structure and dynamics on a microscopic level are summarised below:

- Neutrons are uncharged, which allows them to penetrate the bulk of materials. They interact via the short-rang strong nuclear force with the nuclei of the material under investigation.
- The neutron has a magnetic moment that couples to spatial variations of magnetization on the atomic scale. They are therefore ideally suited to the

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study of magnetic structures, and the fluctuations and excitations of spin systems.

 The energy and wavelength of neutrons may be matched, often simultaneously, to the energy and length scales appropriate for the structure and excitations in condensed matter. The wavelength, λ, is dependent on the neutron velocity following the de Broglie relation:

$$\lambda = \frac{h}{mv} \tag{4.2}$$

where h is Planck's constant (6.636×10^{-34} J s) and v the particle velocity. The associated kinetic energy is:

$$E = \frac{1}{2}mv^2$$
 or $E = \frac{h^2}{2(m\lambda)^2}$ (4.3)

Because their energy and wavelength depend on their velocity it is possible to select a specific neutron wavelength by the time-of-flight technique.

- Neutron do not significantly perturb the system under investigation, so the results of neutron scattering experiments can be clearly interpreted.
- Neutrons are non-destructive, even to delicate biological materials.
- The high-penetrating power of neutrons allows probing the bulk of materials and facilitates the use of complex sample-environment equipment (e.g., for creating extremes of pressure, temperature, shear and magnetic fields).
- Neutrons scatter from materials by interacting with the nucleus of an atom rather than the electron cloud. This means that the scattering power (crosssection) of an atom is not strongly related to its atomic number, unlike Xrays and electrons where the scattering power increases in proportion to the atomic number. Therefore, with neutrons light atoms such as hydrogen (deuterium) can be distinguished in the presence of heavier ones. Similarly, neighbouring elements in the periodic table generally have substantially different scattering cross sections and so can be distinguished. The nuclear dependence of scattering also allows isotopes of the same element to have substantially different scattering lengths for neutrons. Hence isotopic

substitution can be used to label different parts of the molecules making up a material.

4.1.2 Neutron sources

Neutron beams may be produced in two general ways: by nuclear fission in reactor-based neutron sources, or by spallation in accelerator-based neutron sources. A brief description of these processes is given below, with particular reference to the two world's most intense neutron sources, i.e., the Institut Laue-Langevin (ILL) in Grenoble, France [2], and the ISIS Facility at the Rutherford Appleton Laboratory in Didcot, U.K. [3].

• Reactor-based neutron source: neutrons have traditionally been produced by fission in nuclear reactors optimised for high neutron brightness. In this process, thermal neutrons are absorbed by uranium-235 nuclei, which split into fission fragments and evaporate a very high-energy (MeV) constant neutron flux (hence the term "steady-state" or "continuous" source). After the high-energy (MeV) neutrons have been thermalised to meV energies in the surrounding moderator, beams are emitted with a broad band of wavelengths. The energy distribution of the neutrons can be shifted to higher energy (shorter wavelength) by allowing them to come into thermal equilibrium with a "hot source" (at the ILL this is a self-heating graphite block at 2400 K), or to lower energies with a "cold source" such as liquid deuterium at 25 K [4]. The resulting Maxwell distributions of energies have the characteristic temperatures of the moderators (Figure 4.1(a)). Wavelength selection is generally achieved by Bragg scattering from a crystal monochromator or by velocity selection through a mechanical chopper. In this way high-quality, high-flux neutron beams with a narrow wavelength distribution are made available for scattering experiments. The most powerful of the reactor neutron sources in the world today is the 58 MW HFR (High-Flux Reactor) at the ILL.

• Accelerator-based pulsed neutron source: in these sources neutrons are released by bombarding a heavy-metal target (e.g., U, Ta, W), with highenergy particles (e.g., H⁺) from a high-power accelerator – a process known as spallation. The methods of particles acceleration tend to produce short intense bursts of high-energy protons, and hence pulses of neutrons. Spallation releases much less heat per useful neutron than fission (typically 30 MeV per neutron, compared with 190 MeV in fission). The low heat dissipation means that pulsed sources can deliver high neutron brightness – exceeding that of the most advanced steady-state sources – with significantly less heat generation in the target. The most powerful spallation neutron source in the world is the ISIS facility. It is based around a 200 μ A, 800 MeV, proton synchrotron operating at 50 Hz, and a tantalum (Ta) target which releases approximately 12 neutrons for every incident proton. **Figure 4.1** (*a*) Typical wavelength distributions for neutrons from a reactor, showing the spectra from a hot source (2400 K), a thermal source and a cold source (25 K). The spectra are normalised so that the peaks of the Maxwell distributions are unity.

(*b*) Typical wavelength spectra from a pulsed spallation source. The H_2 and CH_4 moderators are at 20 K and 100 K respectively. The spectra have a high-energy "slowing" component and a thermalised component with a Maxwell distribution. Again the spectra are normalised at unity.

(*c*) Neutron flux as a function of time at a steady-state source (grey) and a pulsed source (black). Steady-state sources, such as ILL, have high time-averaged fluxes, whereas pulsed sources, such as ISIS, are optimised for high brightness (not drawn to scale). After [3]



Figure 4.2 Schematic layout of the spallation pulsed neutron source at the Rutherford Appleton Laboratory, ISIS, Didcot, U.K. Beam tubes radiate out from the ISIS target and deliver pulses of "white" neutrons – i.e., neutrons having a wide range of energies – to 18 instruments [3].



- 1. Ion source and pre-injector
- 2. 70 MeV linear accelerator
- 3. 800 MeV synchrotron injection area
- 4. Fast kicker proton beam extraction
- 5. Synchrotron south side
- 6. Synchrotron west side

- 7. Extracted proton beam tunnel
- 8. ISIS target station
- 9. Experimental hall, south side
- 10. Experimental hall, north side
- 11. RIKEN superconducting pion decay line

At ISIS, the production of particles energetic enough to result in efficient spallation involves three stages (see Figure 4.2):

- (1) Production of H⁻ ions (proton with two electrons) from hydrogen gas and acceleration in a pre-injector column to reach an energy of 665 keV.
- (2) Acceleration of the H⁻ ions to 70 MeV in the linear accelerator (Linac) which consists of four accelerating tanks.
- (3) Final acceleration in the synchrotron a circular accelerator 52 m in diameter that accelerates 2.8×10^{13} protons per pulse to 800 MeV. As they enter the synchrotron, the H⁻ ions pass through a very thin (0.3 µm) alumina foil so that both electrons from each H⁻ ion are removed to produce a proton beam. After travelling around the synchrotron (approximately 10000 revolutions), with acceleration on each revolution from electromagnetic fields, the proton beam of 800 MeV is kicked out of the synchrotron towards the neutron production target. The entire acceleration process is repeated 50 times a second.

Collisions between the proton beam and the target atom nuclei generate neutrons in large quantities and of very high energies. As in fission, they must be slowed by passage through moderating materials so that they have the right energy (wavelength) to be useful for scientific investigations. This is achieved by hydrogenous moderators around the target. These exploit the large inelastic-scattering cross-section of hydrogen to slow down the neutrons passing through, by repeated collisions with the hydrogen nuclei. The moderator temperature determines the spectral distributions of neutrons produced, and this can be tailored for different types of experiments (Figure 4.1 (b)). The moderators at ISIS are ambient temperature water (316 K, H₂O), liquid methane (100 K, CH₄) and liquid hydrogen (20 K, H₂).

The characteristics of the neutrons produced by a pulsed source are therefore significantly different from those produced at a reactor (Figure 4.1 (*c*)). The time-averaged flux (in neutrons per second per unit area) of even the most powerful pulsed source is low in comparison with reactor sources.

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However, judicious use of time-of-flight (TOF) techniques that exploit the high brightness in the pulse can compensate for this. Using TOF techniques on the white neutron beam gives a direct determination of the energy and wavelength of each neutron.

4.1.3 SANS instruments

In neutron scattering experiments, instruments count the number of scattered neutrons as a function of wave vector Q, which depends on the scattering angle θ and wavelength λ . For elastic scattering – i.e., when scattered neutrons have essentially identical energy to the incident neutrons – this corresponds to measuring with *diffractometers* the momentum change. Information about the spatial distribution of nuclei can then be obtained in systems ranging in size and complexity from small unit-cell crystals, through disordered systems such as glasses and liquids, to "large-scale" structures such as surfactant aggregates and polymers. *Spectrometers*, on the other hand, measure the energy lost (or gained) by the neutron as it interacts with the sample, i.e., inelastic scattering. These data can then be related to the dynamic behaviour of the sample.

On a reactor source a single-wavelength beam is normally used and monochromatic beams can be produced by wavelength selection by velocity selection through a mechanical chopper. In contrast, on a spallation source polychromatic "white" beams, and a range of wavelengths are used. Energy analysis of the scattered beam is achieved by measuring time-of-flight, i.e., the time the neutrons take to travel from the source to the sample. As a result of the different wavelength spreads, the detectors on reactor and spallation source based instruments differ. For constant λ , the scattering intensity must be measured at different angles to cover the required *Q*-range. This is achieved on reactor sources by varying the sample-to-detector distance, using a moveable detector. On spallation sources, the neutron wavelength varies, and is determined by TOF method, so the position of the detector is fixed. Figures

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4.3 and 4.4 show schematic layout of two typical instruments. More technical details can be found elsewhere [2,3,5].

Figure 4.3 Schematic layout of the LOQ instrument, ISIS spallation source, Didcot, U.K [2]. After interaction with the sample (typical neutron flux at sample = 2×10^5 cm⁻² s⁻¹), the beam passes into a vacuum tube containing an ³H gas filled detector (active area 64×64 cm² with pixel size 6×6 mm²) placed 4.5 m from the sample. Incident wavelengths range ~ 2.2 – 10 Å, and the scattering angle < 7° gives a useful *Q*-range of 0.009 – 0.249 Å⁻¹.



Figure 4.4 Schematic layout of the D22 instrument, ILL reactor source, Grenoble, France [1]. The maximum neutron flux at sample is 1.2×10^8 cm⁻² s⁻¹. D22 possesses the largest area multi-detector (³He) of all small-angle scattering instruments (active area 96 × 96 cm² with pixel size 7.5×7.5 mm²). It moves inside a 2.5 m wide and 20 m long vacuum tube providing sample-to-detector distances of 1.35 m to 18 m; it can be translated laterally by 50 cm, and rotated around its vertical axis to reduce parallax. D22 thus covers a total *Q*-range of up to 1.5 Å⁻¹ for $\lambda = 2.6$ Å (0.85 Å⁻¹ for $\lambda = 4.6$ Å, $\Delta\lambda/\lambda = 5-10$ %).



4.1.4 Scattering theory

Scattering events arise from radiation-matter interactions and produce interference patterns that give information about spatial and/or temporal correlations within the sample. Different modes of scattering may be produced: as mentioned before, scattering may be *elastic* or *inelastic*, but also *coherent* or *incoherent*. Coherent scattering from ordered nuclei produces patterns of constructive and destructive interference that contain structural information, while incoherent scattering results from random events and can provide dynamic information. In SANS, only coherent elastic scattering is considered and incoherent scattering, which appears as a background, can be easily measured and subtracted from the total scattering.

Neutrons interact with the atomic nucleus via strong nuclear forces operating at very short range (~ 10^{-15} m), i.e., much smaller than the incident neutron wavelength (~ 10^{-10} m). Therefore, each nucleus acts as a point scatterer to the incident neutron beam, which may be considered as a plane wave. The strength of interaction of free neutrons with the bound nucleus can

be quantified by the *scattering length*, b, of the atom, which is isotope dependent. In practice, the mean coherent neutron *scattering length density*, ρ_{coh} , abbreviated as ρ , is a more appropriate parameter to quantify the scattering efficiency of different components in a system. As such ρ represents the scattering length per unit volume of substance and is the sum over all atomic contributions in the molecular volume V_m:

$$\rho_{coh} = \frac{1}{V_m} \sum_i b_{i,coh} = \frac{DN_a}{Mw} \sum_i b_{i,coh}$$
(4.4)

where $b_{i,coh}$ is the coherent scattering length of the ith atom in the molecule of mass density D, and molecular weight Mw. N_a is Avogadro's constant. Some useful scattering lengths are given in Table 4.1, and scattering length density for selected molecules in Table 4.1 [6]. The difference in b values for hydrogen and deuterium is significant, and this is exploited in the contrast-variation technique to allow different regions of molecular assemblies to be examined; i.e., one can "see" proton-containing hydrocarbon-type material dissolved in heavy water D₂O.

Nucleus	b / (10 ⁻¹² cm)
¹ Н	-0.3741
² H (D)	0.6671
¹² C	0.6646
¹⁶ O	0.5803
¹⁹ F	0.5650
²³ Na	0.3580
³¹ P	0.5131
³² S	0.2847
CI	0.9577

Table 4.1Selected values of coherent scatteringlength, b [6]

Table 4.2 Coherent scattering length density of selected molecules, ρ , at 25°C [6]. ^{*a*}Value calculated for the deuterated form of the surfactant ion only (i.e., without sodium counterions), and where the tails only are deuterated

	Molecule	ρ / (10 ¹⁰ cm ⁻²)	
Water	H ₂ O	-0.560	
	D ₂ O	6.356	
Heptane	C ₇ H ₁₆	-0.548	
	C ₇ D ₁₆	6.301	
AOT	(C ₈ H ₁₇ COO)CH ₂ CHSO ₃ ⁻ (Na ⁺)	0.542	
	(C ₈ D ₁₇ COO)CH ₂ CHSO ₃ ⁻ (Na ⁺)	5.180 <i>ª</i>	

In neutron scattering experiments the intensity I is measured as a function of a scattering angle, θ , which in the case of SANS is usually less than 10°. Figure 4.5 illustrates schematically a SANS experiment. The incident wave is a plane wave, whose amplitude can be written as [7]:

$$A_{in} = A_o \cos(\underline{k}_o \cdot \underline{R} - \Omega_o t)$$
(4.5)

 A_o is the original amplitude, \underline{k}_o is the wave vector of magnitude $\frac{2\pi}{\lambda}$, \underline{R} is a position vector, Ω_o is the frequency, and t the time. In static experiments, where relative motions of molecules are ignored, there is no time dependence, and if complex amplitudes are considered, equation. 4.5 reduces to:

$$A_{in} = A_{o} \exp(i\underline{k}_{o} \cdot \underline{R})$$
(4.6)

When this wave hits an atom, a fraction of it is scattered, radiating spherically around the scattering centre:

$$A_{sc} = \frac{A_{o}b}{r} \exp(i\underline{k}_{o} \cdot \underline{R})$$
(4.7)

where b is the scattering length and r the distance between two pointscattering nuclei (Figure 4.6*a*). If the atom is not at the origin but at a position vector \underline{R} , the wave scattered in the direction of \underline{k}_s will be phase shifted by $\underline{Q} \cdot \underline{R}$ with respect to the incident wave (Figure 4.6*b*). \underline{Q} is the scattering vector and relates to the scattering angle θ via

$$Q = \underline{\mathbf{k}}_{\mathrm{s}} - \underline{\mathbf{k}}_{\mathrm{o}} \tag{4.8}$$

and the magnitude of $\underline{\underline{\mathcal{Q}}}$ is given by the cosine rule:

$$Q^{2} = k_{o}^{2} + k_{s}^{2} - 2k_{o}k_{s}\cos\theta$$
 (4.9)

Figure 4.5 Schematic instrumental setup of a small-angle scattering experiment. Sample-to-detector distance is usually 1 - 20 m; scattering angle $\theta < 10^{\circ}$.



Figure 4.6 Geometrical relationships in scattering experiments. (*a*) Phase difference between two point scatterers spatially related by the position vector r. The incident and scattered radiation have wave vector k_o and k_s , respectively. For elastic scattering $|k_o| = |k_s| = 2\pi n/\lambda$. (*b*) Determination of the scattering vector $Q = k_s - k_o$, of amplitude $Q = (4\pi/\lambda)\sin(\theta/2)$.



For coherent elastic scattering, $|\mathbf{k}_{o}| = |\mathbf{k}_{s}| = \frac{2\pi n}{\lambda}$, where *n* is the refractive index of the medium, which for neutron is ~ 1, so $|\underline{Q}|$ can be obtained by geometry as:

$$\left|\underline{Q}\right| = Q = 2\left|k_{o}\right|\sin\frac{\theta}{2} = \frac{4\pi}{\lambda}\sin\frac{\theta}{2}$$
 (4.10)

The magnitude Q has dimensions of reciprocal length and units are commonly Å⁻¹; large structures scatter to low Q (and angle) and small structures at higher Q values.

Accordingly, the amplitude of the scattered wave at angle θ for an atom at position <u>R</u> from the origin is:

$$A_{sc} = \frac{A_{o}b}{r} \exp[i(\underline{k}_{o}r - \underline{Q} \cdot \underline{R})]$$
(4.11)

Equation 4.11 is only valid for the simple case where two point scatterers are considered. In the more realistic case of a very large ensemble of atoms present, the total scattered amplitude is then written as:

$$A_{sc} = \frac{A_o}{r} \exp(i\underline{k}_o r) \sum_i b_i \exp(-i\underline{Q} \cdot \underline{R}_i)]$$
(4.12)

In the specific case of SANS and the relevant *Q*-range (distances ~ 10 to 1000 Å, scattering vectors $Q \sim 0.006$ to 0.6 Å⁻¹), dilute samples can be treated as discrete particles dispersed in a continuous medium, and the scattering is controlled by the scattering length density, ρ :

$$\rho(\underline{\mathbf{R}}) = \frac{1}{v} \sum_{j} b_{j} \delta(\underline{\mathbf{R}} - \underline{\mathbf{R}}_{j})$$
(4.13)

where the sum extends over a volume v which is large compared with interatomic distances but small compared to the resolution of the experiment.

Then the scattered amplitude is the Fourier transform of this density in the irradiated volume V:

$$A_{sc}(\underline{Q}) = \int_{V} \rho(\underline{R}) \exp(-i\underline{Q} \cdot \underline{R}) d\underline{R}$$
(4.14)

Radiation detectors do not measure amplitudes as they are not sensitive to phase shift, but instead the intensity I_{sc} of the scattering (or power flux), which is the squared modulus of the amplitude:

$$I_{sc}(\underline{Q}) = \left\langle \left| A(\underline{Q}) \right|^2 \right\rangle = \left\langle A(\underline{Q}) \cdot A^*(\underline{Q}) \right\rangle$$
(4.15)

For an ensemble of n_p identical particles, equation 4.15 becomes [8]:

$$I_{sc}(Q) = n_{p} \left\langle \left\langle \left| A_{sc}(Q)^{2} \right| \right\rangle_{o} \right\rangle_{s}$$
(4.16)

where the ensemble averages are over all orientations, o, and shapes, s.

Therefore, there is a convenient relationship (equation 4.10) between the two instrumental variables, θ and λ , and the reciprocal distance, Q, which is related (via equation 4.14) to the positional correlations r between point scattering nuclei in the sample under investigation. These parameters are related to the scattering intensity I(Q) (equation. 4.16) which is the measured parameter in a SANS experiment, and contains information on intra-particle and inter-particle structure.

4.2 **NEUTRON SCATTERING BY MICELLAR AGGREGATES**

For monodisperse homogeneous spherical particles of radius R, volume V_p , number density n_p (cm⁻³) and coherent scattering length density ρ_p , dispersed in a medium of density ρ_m , the normalised SANS intensity I(*Q*) (cm⁻¹) may be written as [9]:

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$$I(Q) = n_{p} \Delta \rho^{2} V_{p}^{2} P(Q, R) S(Q)$$
 (4.17)

where $\Delta \rho = \rho_p - \rho_m$ (cm⁻²). The first three terms in Equation 4.17 are independent of *Q* and account for the absolute intensity of scattering. A so-called *scale factor*, S_F, can then be defined where:

$$S_{F} = n_{p} (\rho_{p} - \rho_{m})^{2} V_{p}^{2} = \phi_{p} \cdot \Delta \rho^{2} \cdot V_{p}$$

$$(4.18)$$

 ϕ_p is the volume fraction of particles. The scale factor is a measure of the validity and consistency of a model used when analysing SANS data; i.e., the S_F value obtained from model fitting can be compared to the expected value, based on sample composition (from equation 4.18). The last two terms in equation 4.17 are *Q*-dependent functions. P(*Q*,R) is the single particle form factor arising from intra-particle scattering. It describes the angular distribution of the scattering due to the particle shape and size. S(*Q*) is the structure factor arising from inter-particle interactions. To better understand the influence of each term, two scattering profiles are illustrated on Figure 4.7 for the cases of repulsive and attractive forces between interacting homogeneous spheres [8]. It shows how P(*Q*) and S(*Q*) can combine to give the overall intensity I(*Q*). These scattering functions are briefly discussed below.

4.2.1 Single particle form factor P(Q)

P(Q) is the function from which information on the size and shape of particles can be obtained. An approximate representation of the form factor P(Q,R) for spheres is shown in Figure 4.7 In general, it appears as a decay although under high resolution maxima and minima are expected at high Q values. The function P(Q) is usually defined as 1.0 at Q = 0. General expressions of P(Q) are known for a wide range of different shapes such as homogeneous spheres, spherical shells, cylinders, concentric cylinders and discs [7]. For a sphere of radius R:

$$P(Q,R) = \left[\frac{3(\sin QR - QR\cos QR)}{(QR)^3}\right]^2$$
(4.19)

For certain systems such as microemulsions, a polydispersity function may be introduced to account for the particle-size distribution. For spherical droplets, this contribution may be represented by a Schultz distribution function X(R_i) [10, 11], defined by an average radius R^{av} and a root mean square deviation $\sigma = \frac{R^{av}}{(Z+1)^{1/2}}$ with Z a width parameter. P(Q,R) may then be expressed as:

$$P(Q,R) = \left[\sum_{i} P(Q,R_{i})X(R_{i})\right]$$
(4.20)

Figure 4.7 Schematic representation of the particle form P(Q,R) and structure S(Q) factors for attractive and repulsive homogeneous spheres, and their contribution to the scattered intensity I(Q).



P(Q) Form Factor lute non-interacting homogeneous sphere

4.2.2 Structure factor S(Q)

The inter-particle structure factor S(Q) depends on the type of interactions in the system, i.e., attractive, repulsive or excluded volume. For spherical particles with low attractive interactions, a reasonable first approximation is a hard-sphere potential, $S_{hs}(Q)$, given by [12]:

$$S_{hs}(Q) = \frac{1}{1 - n_{p} \cdot f(R_{hs}\phi_{hs})}$$
 (4.21)

where $R_{hs} = R_{core}^{av} + t$ is the hard-sphere radius (with t the hydrocarbon layer thickness) and $\phi_{hs} = \frac{4}{3} \pi R_{hs}^3 n_p$ is the hard-sphere volume fraction. The intensity of scattering (equation 4.17) can then be rewritten as:

$$I(Q) = \phi_{p} \Delta \rho^{2} V_{p} \left[\sum_{i} P(Q, R_{i}) X(R_{i}) \right] S(Q, R_{hs}, \phi_{hs}) \qquad (4.22)$$

As shown in Figure 4.7, $S_{hs}(Q)$ is important at low Q values where it reduces the scattering intensity and produces a peak in I(Q) profile at $Q_{max} = 2\pi/D$, with D the mean nearest neighbour distance in the sample. For dilute, noninteracting, systems $\phi_{hs} \rightarrow 0$, so the structure factor disappears, i.e., $S(Q) \rightarrow 1$. For interacting systems, an effective way of reducing S(Q) is by diluting the system [13], or for charged particles by adding salt [14].

For systems where attractive interactions have to be considered, particularly in the vicinity of phase separation regions or cloud point in binary phase diagrams, a structure factor known as the Ornstein-Zernike (OZ) expression may be used [8]:

$$S_{OZ}(Q) = 1 + \frac{S(0)}{1 + (Q\xi)^2}$$
 (4.23)

where $S(0) = n_p k_B T \chi$, with k_B the Boltzmann constant, T the temperature, and χ the isothermal compressibility. ξ is a correlation length. Far from phase boundaries, $S(0) \rightarrow 0$, and so S_{OZ} (*Q*) disappears, i.e., $S(Q) \rightarrow 1$.

4.2.3 Neutron contrast variation

As mentioned previously, the very different neutron scattering lengths of hydrogen and deuterium are exploited in SANS experiments to reveal details of structure and composition at interfaces. This is routinely applied in microemulsion droplets where different regions can be highlighted by selectively varying the scattering length density of the surfactant, oil or aqueous phase. Three contrasts are commonly studied – core, shell and drop – which can be fitted individually or simultaneously [15]. Figure 4.8 illustrates the scattering length density profiles for a water-AOT-*n*-heptane microemulsion for the three contrasts. The initial situation, where all components are hydrogenated, is shown in Figure 4.8(a). As reported in Table 4.2, the scattering length densities of H₂O, *n*-heptane and AOT are very similar, so that deuteration of the water and/or oil phases allows contrast match of specific regions within the system. The distance from the droplet centre is Z, and so ρ depends on Z owing to the presence of the different materials. Apart from a few subtle effects, such as hydrogen bonding, this isotopic exchange does not usually affect the chemical or physical properties of the system significantly.

Figure 4.8 Elucidation of the structure of water–AOT–*n*-heptane microemulsion droplets by contrast variation. The scattering length density, ρ , depends on Z, the distance from the centre of a droplet.



4.2.4 SANS approximations

A first estimation of the size and shape of particles can be obtained from simple relations between I(Q) and the particle radius (or thickness) based on a few assumptions and/or approximations.

Guinier approximation

The SANS profile I(Q) is very sensitive to different particle shapes. In particular, the Guinier approximation relates the low Q part of the scattering plot to a radius of gyration R_g of the particle. At low Q (Guinier regime), the single particle form factor P(Q,R) for dilute systems simplifies to [16]:

$$P(Q,R) = 1 - \frac{Q^2 R_g^2}{3}$$
(4.24)

where R_g is the root mean square value of the radius averaged over the volume of particle, and relates to the shape of the particle:

- For spheres or cylinders $R_g = \left(\frac{3}{5}\right)^{\frac{1}{2}} R$ (4.25)
- For thin discs $R_g = \frac{R}{4^{\frac{1}{2}}}$ (4.26)
- For long rods $R_g = \frac{L}{12^{\frac{1}{2}}}$ (4.27)

R is the radius of the spheres or cylinders, or disc thickness, and L is the rod length.

Assuming S(Q) = 1 and $1 - X^2 \approx exp(-X^2)$, Equation 4.17 becomes:

$$I(Q) \approx \phi_{p} \Delta \rho^{2} V_{p} \exp\left(-\frac{Q^{2} R_{g}^{2}}{3}\right)$$
(4.28)

The Guinier plot – i.e., ln I(Q) versus Q^2 – should includes a linear section up to the limit $QR_g < 1$. The associated slope is $-\frac{R_g^2}{3}$, and so R_g can be determined

for any isometric particles. Another useful expression for the Guinier approximation is [7, 17]:

$$I(Q) \propto Q^{-D} \exp\left(-\frac{Q^2 R^2}{K}\right)$$
(4.29)

Equations 4.28 and 4.29 are equivalent. They are valid for non-interacting particles (i.e., $S(Q) \rightarrow 1$) only, and over a restricted *Q*-range. The proportionality constant depends on the concentration and isotopic composition. The exponent D is 1 for cylinders, 2 for discs, and 0 for spheres. R is the characteristic dimension of the particle, i.e., the cross sectional radius for cylinders, the thickness for discs, and the radius for spheres. K is an integer of value 4 for cylinders, 12 for discs, and 5 for spheres. Depending on the geometry, the dimension R can be obtained by plotting different quantities against Q^2 :

•	$\ln[I(Q) \cdot Q]$	vs. <i>Q</i> ² :	cylinder radius = $\sqrt{\text{slope} \times 4}$	(4.30)
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•
$$\ln [I(Q) \cdot Q^2]$$
 vs. Q^2 : disk thickness = $\sqrt{\text{slope} \times 2}$ (4.31)

•
$$\ln[I(Q)]$$
 vs. Q^2 ($QR < 1$): sphere radius = $\sqrt{\text{slope} \times 5}$ (4.32)

Therefore the most probable particle shape can be predicted by comparison of the three different I(Q). Q^{D} vs. Q^{2} plots (i.e., the one giving a linear decay).

4.2.5 Porod approximation

At high Q values, the SANS intensity is sensitive to scattering from local interfaces rather than the overall inter-particle correlations. Then I(Q) is related to the total interfacial area S, and the asymptotic intensity (see Figure 4.9) may be analysed using the Porod equation [18, 19]:

$$I(Q) = 2\pi\Delta\rho^2 \left(\frac{S}{V}\right)Q^{-4}$$
(4.33)

where S/V is the total interfacial area per unit volume of solution (cm⁻¹). The Porod equation is only valid for smooth interfaces and a Q-range >> 1/R (Porod

regime). Assuming all the surfactant molecules are located at the interface, the average area per surfactant head group, a_s , can be estimated from:

$$a_{\rm s} = \left(\frac{\rm S/V}{\rm N_{\rm s}}\right) \tag{4.34}$$

where N_s is the number density of surfactant molecules (i.e., surfactant concentration × Avogadro's number). The Porod approximation can also be used to estimate the particle radius [8]. For monodisperse spheres of radius R, a plot of $[I(Q) \cdot Q^4]$ vs. Q gives a first maximum at $Q \approx 2.7/R$ and a minimum at $Q \approx 4.5/R$ (see Figure 4.9).

The Guinier and Porod approximations thus offer simple relations that allow a first estimation of the size and shape of colloidal particles. However, they are limited to dilute, non-interacting systems. As mentioned in the previous section, dilution or addition of salt allow the screening of interactions, so that the assumption S(Q) = 1 in the low Q-range becomes valid and the Guinier approximation can be applied. For microemulsions, these conditions do not always hold, they might be unstable to dilution, and also addition of salt may introduce structural changes. In such cases, information about the size and shape of aggregates are obtained by fitting SANS experimental data to more complex mathematical models, such as those derived for polydisperse spherical droplets and introduced in this section. More details about these models can be found elsewhere [9, 20]. **Figure 4.9** Schematic diagram of a Porod plot for near-monodisperse spheres (see text for details).



Q / Å⁻¹

4.3 NEUTRON REFLECTION

Neutron reflection (NR) is a very useful and reliable method since it provides a direct measure of the surface excess, and also permits structural features of the interface to be elucidated. Just like SANS the only disadvantage is the necessity to carry out expensive experiments at neutron facilities, and in some cases the need for deuterated solvents and/or surfactants. Tensiometry, on the other hand, is a very accessible method but only provides indirect determination of the surface excess via surface tension measurements and application of the Gibbs equation (see Section 2.1.2). Certain material and basic definitions relevant to NR have already been covered in relation to smallangle scattering in section 4.2.

4.3.1 Background theory

The properties of neutrons and their interaction with matter have been presented in Section 4.1 with particular interest in scattering from small particles. Here, reflection of neutrons from a flat surface is considered. The reflectivity profile R(Q) gives information on the structure normal to the interface, and, as with reflection of light, the refractive index, n, normal to the surface is important. For any material n for neutrons is wavelength dependent [21], i.e.,

$$n = 1 - \lambda^2 A + i\lambda C \tag{4.35}$$

where $A = \frac{Nb}{2\pi}$ and $C = \frac{N\sigma_{abs}}{4\pi}$ are constants, with N an atomic number density, b a bound scattering length and σ_{abs} the absorption cross-section (which may often be ignored). Figure 4.10 shows the reflection of a fraction of the incident neutron beam by a smooth surface; the rest being either transmitted or adsorbed. Figure 4.10 Geometry of a neutron reflection experiment and direction of the scattering vector Q_i , where k_o and k_s are the incident and scattered wave vectors, and θ is the scattering angle.





As for SANS, elastic scattering only is considered, i.e., specular reflection, when the moduli of the incident and reflected wave vectors, k_o and k respectively, are equivalent ($|k_o| = |k|$). A scattering vector Q_z defined in one dimension only, i.e., the z direction perpendicular to the sample surface, is then given as:

$$Q_z = \frac{4\pi n}{\lambda} \sin \theta \qquad (4.36)$$

where n is the refractive index. The reflected intensity $R(Q_z)$ is thus measured as a function of Q_z either by varying the wavelength of the neutron beam, λ , and keeping the angle of incidence, θ , constant (method at pulsed neutron sources), or by selecting a constant λ value and varying θ (at reactor sources).

For a plane wave incident upon a surface, if the first medium is air $n_0 \approx 1$, total external reflection occurs below a critical incidence angle $\theta_0 = \theta_c$, and a critical value Q_c , defined by the wavelength λ_c or angle θ_c , is reached. For a clean D_2O surface (Figure 4.11(*a*)) if $\theta < \theta_c$ (i.e., below Q_c) then there is total reflection and R(Q) = 1, whilst above Q_c the reflectivity falls off sharply as Q^4 . The region where R(Q) = 1 is used to determine the instrument calibration scale factor. In the case of a surfactant monolayer on a water sub-phase (Figure 4.11(*b*)), Q_c is usually reached when measurements are made at $\theta < 1.5^\circ$ [8]. On passing through an adsorbed layer the incident neutron beam is partially transmitted and reflected. Waves are reflected from both top and bottom surfaces of the thin interfacial film. There is then an interference between these two reflected beams, resulting in the appearance of a "fringe" in the R(Q) profile. The position of a minimum Q_{min} is related to the layer thickness τ by $Q_{min} \approx 2\pi/\tau$ (Figure 4.11(*b*)).

4.3.2 Layer thickness and adsorbed density

The analysis of specular reflectivity in single- or multiple-layer systems can be done either by comparison with a reflectivity profile calculated using an exact optical matrix method, or by using the kinematic (or Born) approximation method which originates from classical scattering theory.

Figure 4.11 Specular reflection at the sharp interface between two bulk media (*a*), and for a thin interfacial layer (*b*) of thickness d sandwiched between two media. I, R and T are the incident, reflected and transmitted beams respectively. Other symbols as defined in the text. Also illustrated are schematic R(Q) profiles for the two situations.







In the first approach, a characteristic matrix per layer is defined that relates electric vectors in successive layers in terms of Fresnel reflection coefficients – combining refractive index and reflected angle – and phase factors introduced on traversing each layer [22]. A detailed account of this approach can be found in several texts [e.g. 21, 23]. The resulting model typically consists of a series of layers, each with a scattering length density ρ and thickness τ , into which an interfacial roughness between any two consecutive layers can also be incorporated. Indeed most surfaces are affected by a local roughness that reduces the specular reflectivity [24, 25], especially for liquid surfaces where thermally excited capillary waves are present. The calculated and measured profiles are compared, and ρ and τ for each layer varied until the optimum fit is found (determined by a least-squares iterative fitting process). Then secondary parameters such as the area per molecule or the coverage can be easily determined (see below).

Consider the simple situation of a single uniform layer, of thickness d and refractive index n_1 , introduced between bulk media of refractive index n_0 and n_2 (Figure 4.11(*b*)). If the surfactant solution is made up in null reflecting water (NRW), a mixture of 8 mol % D₂O in H₂O where $\rho = 0$ and hence n = 1. Then there is no scattering contribution from the NRW, and reflection arises purely from the surfactant monolayer. Fitting a single-layer model to the data immediately allows the surface excess Γ to be calculated through [26, 27]

$$A_{s} = \frac{\sum b_{i}}{\rho(z)\tau} = \frac{1}{\Gamma N_{a}}$$
(4.37)

where $\sum b_i$ is the sum of scattering lengths over a single molecule, N_a is Avogadro's number, and $\rho(z)$ and τ are the optimised scattering length density and layer thickness determined by fitting. The absolute value of τ is model dependent and will vary with the choice of the distribution function employed to describe the scattering length density profile normal to the surface. However, as described by Simister *et al.* [28], the sets of $\rho(z)$ values required to give a good fit exactly compensate for the change in τ so that A_s is independent of the uncertainty in τ .

A second analysis method is the kinematic (or Born) approximation [29]. In this approach, the reflectivity $R(Q_z)$ is related to the scattering length density profile normal to the interface, $\rho(z)$, by

$$R(Q_z) = \frac{16\pi^2}{Q_z^2} |\hat{\rho}(Q_z)|^2$$
(4.38)

where $\hat{\rho}(Q_z)$ is the one-dimensional Fourier transform of $\rho(z)$,

$$\hat{\rho}(Q_z) = \int_{-\infty}^{+\infty} \exp(-iQ_z z)\rho(z)dz \qquad (4.39)$$

4.3.3 Partial structure factor analysis

Details of the development of the kinematic approximation for the study of adsorbed thin films are described elsewhere [29, 30]. For surfactant monolayers adsorbed at the air–solution interface, the main features of interest – in addition to film thickness and surface coverage – are the relative positions of the chains, head, and water, and the widths of their distributions normal to the interface. Such structural features can be obtained through analysis of complementary R(Q) profiles, determined at different isotopic compositions using hydrogen/deuterium labeling of the surfactant. This is known as a partial structure factor (PSF) analysis, which is valid under the kinematic approximation. Depending on the labeling scheme, the total scattering may be expressed in terms of numerous partial structure factors that are descriptive of the various components in the interface [29, 31]. Below is a brief description of such analysis where a simple binary system consisting of a surfactant solute, A, and a solvent, S, are considered. Then the scattering length density may be represented as

$$\rho(z) = N_{s}(z)b_{s} + N_{A}(z)b_{A}$$
(4.40)

where $N_A(z)$ and $N_S(z)$ are the number densities of solute and solvent respectively and b_i are the scattering lengths. Combining equations 4.38 and 4.40 gives

$$R(Q_z) = \frac{16\pi^2}{Q_z^2} \left[b_A^2 h_{AA} + b_S^2 h_{SS} + 2b_A b_S h_{AS} \right]$$
(4.41)

where the h_{ii} and h_{ij} are the PSFs : h_{ii} are self-terms that contain information about distributions of the individual components, and are one-dimensional Fourier transforms of $N_i(z)$:

$$h_{ii}(Q_z) = |N_i(Q_z)|^2$$
 (4.42)

 h_{ij} are cross-terms that describe the relative positions of the different components. In the example given here, of a surfactant solute and solvent, assuming that the distributions of A and S at the interface are exactly even (symmetrical about the centre) and odd respectively [32], then the following relationship holds,

$$h_{AS} = \pm (h_{AA} h_{SS})^{1/2} \sin(Q_z \delta_{AS})$$
 (4.43)

where δ is the separation between the centres of the surfactant and solvent distributions. The distributions may not be exactly even/odd, and deviations from this assumption may affect the accuracy with which δ_{AS} can be determined. Circumstances where this approximation fails has been discussed in full elsewhere [33], but this is not expected to arise for simple surfactants [34, 35].

In principle, the $N_i(z)$ can be obtained by Fourier transformation of the PSFs, but in practice, an analytical function that best represents the form of

 $N_i(z)$ is assumed. The function is then Fourier transformed and fitted to the experimental data. For monolayer of soluble surfactants, it is shown that a Gaussian distribution is a good representation of the number density profile, $N_A(z)$, [36]:

$$N_{A}(z) = N_{A0} \exp\left(\frac{-4z^{2}}{\sigma_{A}^{2}}\right)$$
 (4.44)

where N_{A0} is the maximum number density and σ_A is the full width at the 1/e of the maximum number density. The total adsorbed amount in the monolayer, Γ_m , is related to N_{A0} through

$$\Gamma_{\rm m} = \frac{1}{A_{\rm s}} = \frac{\sigma_{\rm A} N_{\rm A0} \pi^{1/2}}{2}$$
(4.45)

where A_s is the area per molecule.

For the interfacial solvent distribution, a convenient analytical form is the tanh function given by

$$N_{s} = N_{s0} \left[\frac{1}{2} + \frac{1}{2} \tanh\left(\frac{z}{\zeta}\right) \right]$$
(4.46)

where N_{S0} is the number density of water in the bulk solution and ζ is the width parameter. The respective PSFs for distributions described by equations 4.44 and 4.46 are then

$$Q_{z}^{2}h_{AA} = \frac{\pi \sigma_{A}^{2}N_{A0}^{2}Q_{z}^{2}}{4} \exp\left(-\frac{Q_{z}^{2}\sigma_{A}^{2}}{8}\right)$$
(4.47)

$$Q_{z}^{2}h_{ss} = \frac{N_{s0}^{2}\zeta^{2}\pi^{2}Q_{z}^{2}}{4} \operatorname{cosech}^{2}\left(\frac{\zeta\pi Q_{z}}{2}\right)$$
 (4.48)

The cross PSF, h_{AS} , can be obtained directly by combining the above equations for h_{AA} and h_{SS} into equation 4.43 and fitting the resulting function for δ_{AS} :

$$Q_{z}^{2}h_{AS} = \frac{\sigma_{A}N_{S0}N_{A0}\pi^{3/2}\zeta Q_{z}^{2}}{4} \exp\left(-\frac{Q_{z}^{2}\sigma_{A}^{2}}{16}\right) \cosh \left(\frac{\zeta \pi Q_{z}}{2}\right) \sin \pi \delta_{AS} \quad (4.49)$$

Structural parameters (with the exception of δ_{AS}) obtained from the kinematic approximation are dependent upon the assumed distribution shapes. For the solute, however, it can be shown that the surface coverage, Γ_m , is independent of any assumptions made about the N_A(z) distribution [29]. For a monolayer with a Gaussian distribution at the surface of water that is contrast matched to air, NRW, the reflectivity is given by [37, 38].

$$\frac{Q_{z}^{2}R(Q_{z})}{16\pi^{2}} \approx (\Gamma_{m}N_{a}b_{A})^{2} \exp(-Q_{z}^{2}\sigma_{A}^{2})$$
(4.50)

where N_a is the Avogadro constant. Hence, a plot of $\ln Q_z^2 R(Q_z)$ vs. Q_z^2 extrapolated to $Q_z = 0$ yields a model independent value for Γ_m .

The kinematic approximation assumes all scattering is due to single events, i.e., effects of multiple scattering within the sample are ignored. Therefore this approximation is only valid when the scattering is weak, that is, the incident intensity, I_0 is much greater than the scattered intensity, I_s . When applied to reflection, the approximation breaks down in the region $Q \sim Q_c$ since $I_s \sim I_0$, and the scattering is no longer "weak". Thus interpretation of reflectivity data using the kinematic theory is strictly only valid far from the region of total reflection. As a result, equation 4.38 is only approximate and fails at low Q. To utilize the entire range of reflectivity data available, and to account for the failure of the kinematic approximation as $Q_z \sim Q_c$, each calculated $R(Q_z)$ needs to be corrected before being compared with the observed reflectivity [27, 39].

An excellent review of the applications of neutron reflectometry has been published [40].

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