



Combining wide-angle and small-angle scattering to study colloids and self-assembly



Karen J. Edler^{a,*}, Daniel T. Bowron^b

^a Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, UK

^b ISIS, Science and Technology Facilities Council, Rutherford Appleton Laboratory, Harwell Oxford, Didcot OX11 0QX, UK

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ABSTRACT

The characterization of structure over a wide range of length scales from atomic to microns is a common requirement for understanding the behaviour of many soft matter systems. In the case of self-assembling and colloidal materials, the final properties will depend sensitively on intermolecular as well as interparticle interactions. Experimental methods such as wide and small angle scattering, which, between them, cover a wide range of length-scales are therefore growing in importance to better understand and thus exploit these systems. This review covers the growing use of wide angle scattering, either in conjunction with small angle scattering, or applied to systems which have previously been studied using small angle scattering, in order to highlight the complementarity between these two techniques, and the areas where atomistic information has contributed to understanding of the behaviour of systems containing structure at much larger length scales.

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1. Introduction

Small and wide-angle neutron scattering are each separately well-established techniques for characterization of solution structures. Small angle neutron scattering (SANS) measures structures in a size range from roughly 1 nm to several hundreds of nm, depending on the angle range measured [1,2]. It is widely used in the study of a range of colloidal systems from nanoparticles, to micelles and biomolecules in solution. Wide-angle neutron scattering, on the other hand, measures the correlations between molecules in solution on length scales similar to that of crystallography, giving atomic level descriptions of average molecular arrangements within the fluid. Typically wide-angle scattering has seen greater application in the study of molecular liquids, solvation shells and glassy materials, but it is increasingly being used to study more complex molecules and molecular assemblies. Increases in computational power have enabled modelling of larger systems containing bigger molecules or aggregations of molecules, leading to the ability to analyse experimental results covering wider length scales, up to, and now matching to some degree, those sizes typically

covered by the small-angle scattering technique. The two techniques are complementary, and potentially overlap in their descriptions of structure, but until recently there has been very little intersection in their application to colloidal and self-assembled systems.

In this review we discuss the recent application of both SANS and wide-angle scattering to a range of materials that has developed over roughly the last twenty years. We have restricted our discussion to systems that do not contain crystalline ordering, as studies of systems showing crystalline or liquid crystalline diffraction peaks alongside nanostructural features are not uncommon. We focus instead on liquid and disordered particulate systems, which do not have strong diffraction features in either wide or small angles. We aim to highlight the complementarity between wide and small angle scattering and demonstrate how a multi-length scale structural understanding of complex soft matter systems can be obtained which enables better insights into function and properties than either technique would alone.

2. Techniques & theory

In scattering techniques the intensity and shape of the scattered signal arises from density differences in the sample [1,2]. In the case of neutron scattering, since neutrons interact with atomic nuclei, the scattering pattern reflects the distribution of different isotopes within the sample as well as their physical arrangement in space. In the discussion that follows, the scattering from a sample is measured as a function of Q ,

* Corresponding author.

E-mail addresses: k.edler@bath.ac.uk (K.J. Edler), daniel.bowron@sfc.ac.uk (D.T. Bowron).

the magnitude of the momentum transfer vector of the scattering process. This is defined as:

$$Q = \frac{4\pi}{\lambda} \sin \theta \quad (1)$$

where λ is the wavelength of the neutron incident upon the sample, and 2θ is the scattering angle.

In small angle scattering, the length scales measured are much larger than individual molecules. Therefore average material properties can be used when analysing the data. The physical density and the neutron scattering length for the elements in the sample are therefore combined in the scattering length density, Nb :

$$Nb = \frac{N_A \cdot \rho}{MW} \sum_i b_i \quad (2)$$

where ρ is the mass density, MW is the molecular weight and b_i is the neutron scattering length for the isotopes present. For small angle scattering from colloids or self-assembled micellar or lipid systems, the data is usually modelled in terms of objects with defined shape (e.g. sphere, cylinder, core-shell ellipsoid), interacting with each other in a solvent (Fig. 1). A collection of such models can be found in reference [3]. Scattering length densities can therefore be calculated for the shape, or regions of the shape in the sample (eg for a nanoparticle or for the solvent). The shape term is designated the form factor ($F(Q)$), whilst interactions between objects are described by the structure factor ($S(Q)$). For a system containing monodisperse, spherically-symmetric particles, the scattered intensity $I(Q)$ can then be expressed as:

$$I(Q) = N_p V_p^2 (Nb_p - Nb_s)^2 F(Q)S(Q) + B_{inc} \quad (3)$$

where N_p is the number of particles, V_p is the volume of the particles, Nb_p and Nb_s are the scattering length densities of the particle and solvent respectively, whilst B_{inc} is the incoherent background scattering. More complicated approaches are needed for polydisperse and/or

non-spherosymmetric particle systems. [4] SANS is a low-resolution technique since a typical measurement will span roughly a Q range of 0.007 to 0.3 \AA^{-1} , meaning that molecular details cannot be resolved.

In contrast to the case of small angle scattering, wide angle scattering from liquids or non-crystalline systems is typically measured over a Q -range from $\leq 0.1 \text{ \AA}^{-1}$ to $\geq 20 \text{ \AA}^{-1}$, and consequently probes structural correlations in the sample with atomic resolution or better. The experiments themselves measure the total structure factor, $S(Q)$, which is defined via the atomic structure as: [5]

$$S(Q) - 1 = \frac{1}{\left(\sum_{\alpha} c_{\alpha} \langle b_{\alpha} \rangle\right)^2} \sum_{\alpha} \sum_{\beta \geq \alpha} (2 - \delta_{\alpha\beta}) c_{\alpha} c_{\beta} \langle b_{\alpha} \rangle \langle b_{\beta} \rangle [S_{\alpha\beta}(Q) - 1]. \quad (4)$$

c_{α} and c_{β} are the atomic concentrations of atoms of type α and β in the sample, and $\langle b_{\alpha} \rangle$ and $\langle b_{\beta} \rangle$ are the corresponding bound coherent scattering lengths of the atomic elements or if appropriate, their isotopes. $S_{\alpha\beta}(Q)$ are the Faber–Ziman partial structure factors [6] describing the pair correlations between atoms of type α and β , and $\delta_{\alpha\beta}$ is the Kronecker delta function to avoid double counting the like-atom correlations.

As the experiment is atomistic in nature there is no need to include a form factor to encode particle shapes within the measured total structure factor, and instead data is generally analysed in terms of the related total radial distribution function, $G(r)$. This is obtained from the structure factor via the well-known Fourier transform:

$$G(r) - 1 = \frac{1}{(2\pi)^3 \rho_0} \int_0^{\infty} 4\pi Q^2 (S(Q) - 1) \frac{\sin Qr}{Qr} dQ. \quad (5)$$

where ρ_0 is the atomic density of the sample. The total pair distribution function is formed from the sum of the Faber–Ziman atomic site-site partial pair distribution functions, $g_{\alpha\beta}(r)$, in the same way as the

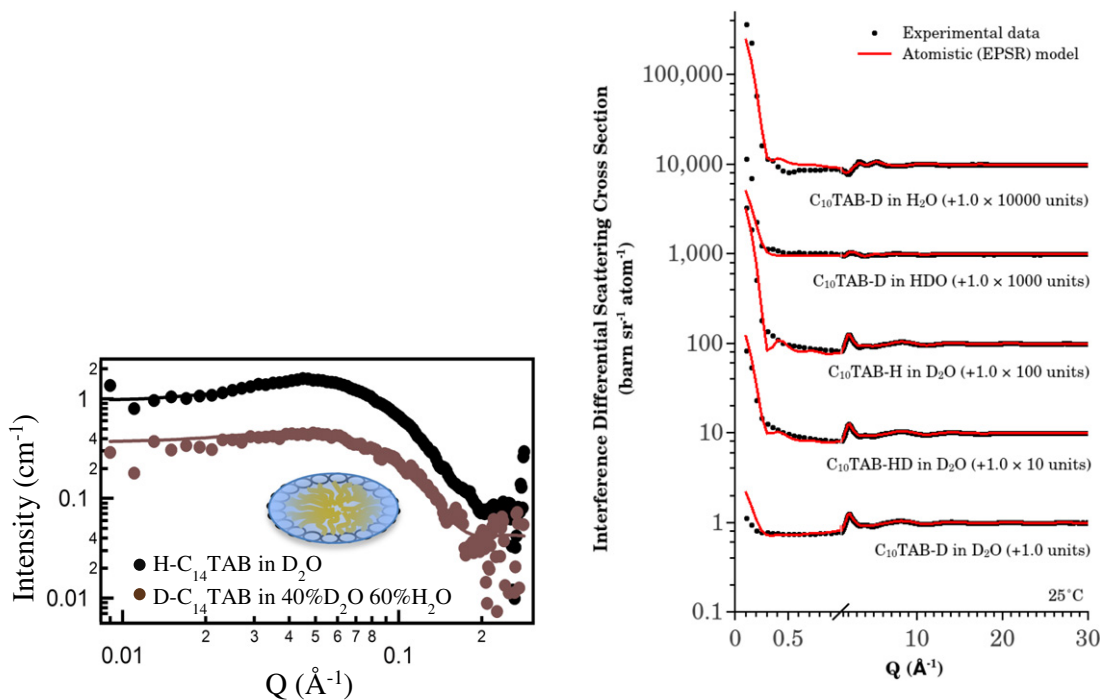


Fig. 1. (left) Example of small angle scattering data from 0.037 M tetradecyltrimethylammonium bromide micelles in water in the presence of the water soluble polyelectrolyte polyethylenimine ($M_w \sim 2000$, 3 wt%), fitted to a low resolution uniform ellipsoid model, with a repulsive charged-sphere structure factor [52] (right) Wide angle scattering data from multiple neutron contrasts fitted to an atomistic model of surfactant molecules in water, arranged into micelle clusters as shown in Fig. 3.

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