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Incoherent neutron scattering from multi-element materials

Charles J. Glinka

University of Delaware, Newark, DE 19716 , USA, and Center for Neutron Research, NIST, 100 Bureau Drive, Gaithersburg, MD 20899-6102, USA. Correspondence e-mail: charles.glinka@nist.gov

In a neutron diffraction measurement, including small-angle scattering, there is generally a featureless (*i.e.* Q-independent) component due to incoherent scattering. This scattering contains no information about the atomic structure or structure on any scale. There may also be featureless scattering that arises from atomic disorder in multi-element materials. This scattering is sometimes referred to as compositional or mixture incoherent scattering. However, this designation is misleading. A much better designation is diffuse coherent scattering. Here the differences and distinguishing characteristics of incoherent scattering *vis-à-vis* diffuse coherent scattering due to atomic disorder are delineated and demonstrated experimentally.

1. Introduction

Most textbooks on neutron scattering discuss the concept of incoherent scattering in detail only for materials consisting of a single atomic species (*e.g.* Bacon, 1962; Squires, 1978; Roe, 2000). Such discussions are adequate for introducing the concepts of nuclear spin incoherence and isotopic incoherence. Most materials, however, consist of more than one atomic species and hence the question arises as to how to calculate the incoherent contribution to the scattering from such materials.

When considering the neutron scattering from a multi-element material, whether it be a compound, a solid or liquid solution, or a molecular solid or liquid, it is important to distinguish between the incoherent scattering and any diffuse coherent scattering that may be present and is related to the degree of atomic disorder in the material. In the extreme case of complete atomic disorder, there will in general be a component of the coherent scattering that is essentially Q independent, similar to the true incoherent scattering that arises from the isotopic and nuclear spin distributions.

1.1. Scattering formalism

The scattering cross section from a system of N atoms in a volume V is given in the Born approximation by

$$\frac{\mathrm{d}\Sigma_\mathrm{s}}{\mathrm{d}\Omega} = \frac{1}{V}\left\langle \left| \sum_i^N b_i \exp(i\mathbf{Q}\cdot\mathbf{r}_i) \right|^2 \right\rangle$$
$$= \frac{1}{V}\left\langle \sum_{i,j}^N b_i b_j \exp\left[i\mathbf{Q}\cdot(\mathbf{r}_i - \mathbf{r}_j)\right] \right\rangle, \qquad (1)$$

where the angle brackets denote averaging over an ensemble of equivalent systems.[1] In this expression, b_i is the scattering

[1] Equivalent systems refer to all possible configurations of the atoms, including their nuclear isotopes and spin states, which may affect the scattering of a neutron beam incident on a sample.

length of the atom at location $\mathbf{r}_i$. If all of the atoms are of a single atomic species (*i.e.* a single element), then the ensemble average can clearly be written as

$$\frac{1}{V}\left\langle \sum_{i,j}^N b_i b_j \exp\left[i\mathbf{Q}\cdot(\mathbf{r}_i - \mathbf{r}_j)\right] \right\rangle = \frac{1}{V}\sum_{i,j}^N \langle b_i b_j\rangle\langle\exp\left[i\mathbf{Q}\cdot(\mathbf{r}_i - \mathbf{r}_j)\right]\rangle, \qquad (2)$$

because there is no correlation between an atom's location and the isotope or nuclear spin state at that location. What may be less obvious is that equation (2) also applies when there is more than one type of atomic species in the sample. In that case, there is, in general, a correlation between a given location and the type of atom at the location. However, even though a given site may be more likely to be populated by one type of atom than another, there is still no correlation with a particular isotope or nuclear spin state of that atomic species at that site. Hence equation (2) remains valid even for multi-element materials.

For the same reasons the average of the product of scattering lengths can be written as

$$\langle b_i b_j\rangle = \langle b_i\rangle\langle b_j\rangle + \delta_{i,j}\left(\langle b_i^2\rangle - \langle b_i\rangle\langle b_j\rangle\right), \qquad (3)$$

so that equation (2) becomes

$$\frac{\mathrm{d}\Sigma_\mathrm{s}}{\mathrm{d}\Omega} = \frac{1}{V}\left\{ \sum_i^N \langle b_i^2\rangle + \sum_{\substack{i,j \\ i\neq j}}^N \langle b_i\rangle\langle b_j\rangle \exp\left[i\mathbf{Q}\cdot(\mathbf{r}_i - \mathbf{r}_j)\right] \right\},$$

$$\frac{\mathrm{d}\Sigma_\mathrm{s}}{\mathrm{d}\Omega} = \frac{1}{V}\left\{ \left| \sum_i^N \langle b_i\rangle \exp(i\mathbf{Q}\cdot\mathbf{r}_i) \right|^2 + \sum_i^N \left(\langle b_i^2\rangle - \langle b_i\rangle^2\right) \right\}. \qquad (4)$$

Only the first term in equation (4) contains information about the arrangement, or structure, of the atoms. This term is called the coherent scattering:

$$\frac{d\Sigma_{coh}}{d\Omega} = \frac{1}{V} \left| \sum_i^N \langle b_i \rangle \exp(i\mathbf{Q} \cdot \mathbf{r}_i) \right|^2. \tag{5}$$

The second term in equation (4) contains no structural information and is called the incoherent scattering:

$$\frac{d\Sigma_{incoh}}{d\Omega} = \frac{1}{V} \sum_i^N \left(\langle b_i^2 \rangle - \langle b_i \rangle^2 \right). \tag{6}$$

To reduce equation (4) further to a useful form for computations, one must indicate how many of each type of atom is present in V. If there are, say, m elements represented, and N_j atoms of element j, then the fraction of atoms of type j is

$$f_j = N_j/N \quad \text{where} \quad N = \sum_j^m N_j \quad \text{and, therefore,} \quad \sum_j^m f_j = 1. \tag{7}$$

Now if all the atoms are disordered, then

$$\langle b_i \rangle = \langle b \rangle = \sum_j^m f_j \langle b_j \rangle \quad \text{and} \quad \langle b_i^2 \rangle = \langle b^2 \rangle = \sum_j^m f_j \langle b_j^2 \rangle. \tag{8}$$

Substituting equation (8) into equation (4) leads to

$$\frac{d\Sigma_s}{d\Omega} = \frac{N}{V} \left[\frac{\langle b \rangle^2}{N} \left| \sum_i^N \exp(i\mathbf{Q} \cdot \mathbf{r}_i) \right|^2 + \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}}^m f_i f_j \left(\langle b_i \rangle - \langle b_j \rangle \right)^2 \right. $$
$$\left. + \sum_j^m f_j \left(\langle b_j^2 \rangle - \langle b_j \rangle^2 \right) \right]. \tag{9}$$

Notice the similarities, and differences, between equations (9) and (4). The first and third terms of equation (9) correspond to the first and second terms of equation (4), and represent coherent and incoherent scattering, respectively. It is the middle term in equation (9) that is new, arising from the presence of more than one element, and, more importantly, the assumption that the atoms are randomly distributed among the available sites. This term is Q independent and thus is sometimes referred to as compositional or mixture incoherent (Cotton, 1991; Brûlet *et al.*, 2007) scattering. A better designation, however, is diffuse coherent scattering: diffuse because of the lack of Q dependence, and coherent because this term provides information about the structure of the system, namely, that the atoms are disordered. It may at first seem odd to refer to disorder as a type of structure, yet that is exactly what it is. The essence of the assumption leading to equation (9) is that there is no correlation between the type of atom occupying a given site and the type occupying any other site, which is, in fact, a strong statement about the structure of the system: quite strong, for as we shall see, it does not apply to most real materials.

2. Specific examples

2.1. NaCl

Consider polycrystalline NaCl, a system with two atomic species (A and B), which has a face-centered-cubic crystal structure with mass density $\rho = 2.165$ g cm^{-3}, molecular weight $M_W = 58.44$ and $N/V = 1/v_m = 2.231 \times 10^{22}$ molecules cm^{-3} (v_m

is the molecular volume). For such a material, the coherent cross section, from equation (5) becomes

$$\frac{d\Sigma_{coh}}{d\Omega} = \frac{1}{V} \left| \sum_i^{N_A+N_B} \langle b_i \rangle \exp(i\mathbf{Q} \cdot \mathbf{r}_i) \right|^2 \rightarrow \frac{N}{V} |F_{hkl}|^2 \delta(\mathbf{Q} - \mathbf{G}_{hkl}), \tag{10}$$

where $\mathbf{G}_{hkl} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$ is a reciprocal lattice vector, $F_{hkl} = \sum_n \langle b \rangle_n \exp[2\pi i(hx_n + ky_n + lz_n)]$ is the structure factor for the hkl Bragg reflection and the sum is over the atoms in the unit cell. For the NaCl rock salt structure,

$$
\begin{aligned}
F_{hkl} &= 4(b_{c,Cl} + b_{c,Na}) \quad &\text{for } hkl \text{ all even,} \\
F_{hkl} &= 4(b_{c,Cl} - b_{c,Na}) \quad &\text{for } hkl \text{ all odd,} \\
F_{hkl} &= 0 \quad &\text{for } hkl \text{ mixed.}
\end{aligned}
\tag{11}
$$

The bound coherent scattering lengths, $\langle b \rangle = b_c$, are $b_c(\text{Na}) = 3.63$ fm and $b_c(\text{Cl}) = 9.566$ fm (Sears, 1992).

The incoherent cross sections for each element are (Sears, 1992)

$$
\begin{aligned}
\sigma_{incoh} = 4\pi(\langle b^2 \rangle - \langle b \rangle^2) &= 1.62 \text{ barns (Na)} \\
&= 5.3 \text{ barns (Cl)}
\end{aligned}
\tag{12}
$$

(1 barn $= 10^{-28}$ m^2). Hence the corresponding macroscopic cross section is

$$\Sigma_{incoh} = (N/V) \sum_i \sigma_{incoh} = 0.1544 \text{ cm}^{-1}. \tag{13}$$

For hypothetical disordered NaCl, in which the sites in the rock salt structure are occupied at random by either Na or Cl, the first term in equation (9) gives

$$F_{hkl} = \langle b \rangle \sum_n \exp[2\pi i(hx_n + ky_n + lz_n)],$$
$$\text{where } \langle b \rangle = (b_{c,Cl} + b_{c,Na})/2, \tag{14}$$

and

$$
\begin{aligned}
F_{hkl} &= 2(b_{c,Cl} + b_{c,Na}) \quad &\text{for } hkl \text{ all even or all odd,} \\
F_{hkl} &= 0 \quad &\text{for } hkl \text{ mixed.}
\end{aligned}
\tag{15}
$$

In addition, there is the diffuse coherent scattering [second term in equation (9); this diffuse scattering due to site disorder is called the Laue monotonic scattering (Warren, 1969)],

$$
\begin{aligned}
\frac{d\Sigma_{c,Laue}}{d\Omega} &= \frac{N}{V} \frac{1}{2} (b_{c,Cl} - b_{c,Na})^2, \\
\Sigma_{c,Laue} &= 4\pi \frac{d\Sigma_{c,Laue}}{d\Omega} = 0.050 \text{ cm}^{-1},
\end{aligned}
\tag{16}
$$

as well as the incoherent scattering,

$$\Sigma_{incoh} = (N/V) \sum_i \sigma_{incoh} = 0.1544 \text{ cm}^{-1}. \tag{17}$$

These two cases are summarized in Fig. 1 (where the multiplicity factors for the individual Bragg peaks have been ignored to emphasize the structure factors).

2.2. H₂O

From equation (6), the macroscopic incoherent scattering cross section for light water is

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Table 1
The mean and mean-square scattering lengths for hydrogen and oxygen (Sears, 1992).

Element	$\langle b \rangle$ ($\times 10^{-12}$ cm)	$\langle b^2 \rangle = \sigma_s/4\pi$ (barns)
Hydrogen	−0.374	6.53
Oxygen	0.580	0.337

$$\Sigma_{\mathrm{incoh}} = \frac{4\pi N}{V} \sum_{j=1}^{2} f_j \left(\langle b_j^2 \rangle - \langle b_j \rangle^2 \right)$$

$$= \frac{1}{V} \sum_{j=1}^{2} N_j \sigma_{\mathrm{incoh},j} = \sum_{j=1}^{2} n_j \sigma_{\mathrm{incoh},j}, \quad (18)$$

where $\sigma_{\mathrm{incoh},j} = 4\pi(\langle b_j^2 \rangle - \langle b_j \rangle^2)$ and n_j is the number density of atoms of type j.

Using the values in Table 1, and $n_{\mathrm{H}} = 2 (\rho N_A/\mathrm{MW}) = 6.69 \times 10^{22}$ atoms of H per cm^{-3} ($n_O = 3.35 \times 10^{22}$ per cm^{-3}; N_A is Avogadro's number) yields

$$\Sigma_{\mathrm{incoh}}(\mathrm{H_2O}) = 5.37 \ \mathrm{cm}^{-1} \quad (19)$$

This cross section is calculated using the bound scattering lengths for the nuclei. The actual cross section for water depends on the incoming neutron energy and the water

Sodium Chloride
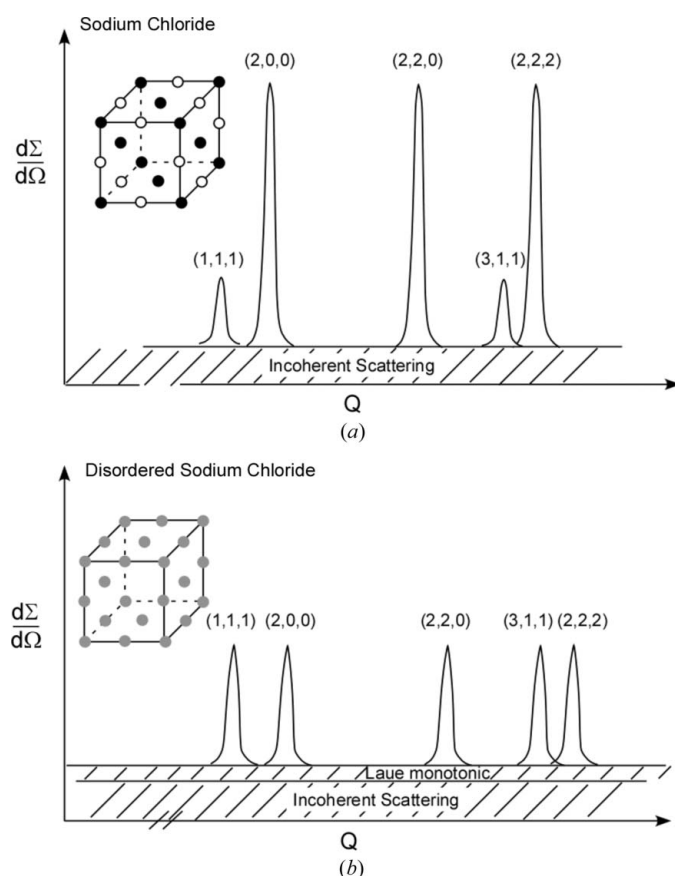
(a)

Disordered Sodium Chloride

(b)

Figure 1
Depiction of the neutron scattering from polycrystalline NaCl including the Q-independent incoherent scattering (a). If the Na and Cl atoms were completely disordered (b) there would be additional diffuse coherent scattering as a result of the atomic disorder.

temperature. The measured incoherent scattering cross section from water is, for example, ~5.7 cm^{-1} for 5 meV neutrons at 290 K, and ~7.7 cm^{-1} for 1 meV neutrons at 290 K (Brookhaven National Laboratory, 1976, hereafter denoted BNL 325).

What about the other Q-independent term in equation (9)? Should the middle term in equation (9)[2] be added to the result obtained in equation (18) to give the 'total incoherent scattering'? The answer is no, because the assumption leading to equation (9) that any atom is equally likely to occupy any available site does not apply to a molecular liquid like water. [For equation (9) to apply to water, all possible molecular permutations (H_2O, HO_2, H_3 and O_3) would have to be present in the liquid.]

Another way to obtain this result [equation (18)] for the incoherent scattering, and one that will give additional insight when we consider H_2O/D_2O mixtures next, is to treat the water molecule as the primary scattering entity. This approach is valid at low Q where the internal structure of the molecule is unresolvable ($Q r_m \ll 1$, where r_m is any intramolecular distance).

We start again from equation (1) and proceed as before to equation (4),

$$\frac{\mathrm{d}\Sigma_s}{\mathrm{d}\Omega} = \frac{1}{V} \left\langle \left| \sum_{i}^{N_m} b_i \exp(i\mathbf{Q} \cdot \mathbf{r}_i) \right|^2 \right\rangle$$

$$= \frac{1}{V} \langle b \rangle^2 \left| \sum_{i}^{N_m} \exp(i\mathbf{Q} \cdot \mathbf{r}_i) \right|^2 + \frac{N_m}{V} \left(\langle b^2 \rangle - \langle b \rangle^2 \right), \quad (20)$$

where N_m is the number of molecules in volume V,

$$\langle b \rangle = 2\langle b_H \rangle + \langle b_O \rangle \quad (21)$$

and

$$\langle b^2 \rangle = \langle (b_{H_1} + b_{H_2} + b_O)^2 \rangle$$
$$= 2\langle b_H^2 \rangle + \langle b_O^2 \rangle + 4\langle b_H \rangle \langle b_O \rangle + 2\langle b_H \rangle^2. \quad (22)$$

Hence

$$\langle b^2 \rangle - \langle b \rangle^2 = 2\left(\langle b_H^2 \rangle - \langle b_H \rangle^2 \right) + \left(\langle b_O^2 \rangle - \langle b_O \rangle^2 \right) \quad (23)$$

and

$$\frac{\mathrm{d}\Sigma_{\mathrm{incoh}}}{\mathrm{d}\Omega} = \frac{3 N_m}{V} \sum_{j=1}^{2} f_j \left(\langle b_j^2 \rangle - \langle b_j \rangle^2 \right), \quad (24)$$

which is equivalent to equation (18).

2.3. H$_2$O/D$_2$O mixtures (not including H/D exchange)

Since H_2O/D_2O mixtures are used extensively to control scattering contrast in aqueous solutions, this is an important case to consider. At low Q, we can again treat the individual water molecules as the primary scattering entities (thereby

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[2] The middle term in equation (9) integrated over dΩ for H_2O would be $\Sigma_{\mathrm{Laue}} = 4\pi n f_H f_O (\langle b_H \rangle - \langle b_O \rangle)^2$, where n is the number of atoms per unit volume. For $f_H = 2/3$, $f_O = 1/3$, $\langle b_H \rangle = -3.74$ fm, $\langle b_O \rangle = 5.8$ fm and $n = 3(3.35 \times 10^{22})$ atoms cm^{-3}, $\Sigma_{\mathrm{Laue}} = 0.255$ cm^{-1}.

ignoring their internal structure) as discussed in the previous section. We start again from equation (1), written as

$$\frac{d\Sigma_s}{d\Omega} = \frac{1}{V}\left\langle \left|\sum_i^{N_m} b_i \exp(i\mathbf{Q}\cdot\mathbf{r}_i)\right|^2 \right\rangle$$

$$= \frac{1}{V}\left\langle \sum_i^{N_m}\sum_j^{N_m} b_i b_j \exp[i\mathbf{Q}\cdot(\mathbf{r}_i - \mathbf{r}_j)] \right\rangle, \quad (25)$$

where N_m is the number of molecules in the volume V, $\mathbf{r}_i$ is the position (*e.g.* the center of mass) of molecule i and b_i is the scattering length for the molecule.

If we assume there is no correlation between a site, $\mathbf{r}_i$, and the type of molecule, H_2O or D_2O, at that site, then equation (25) can be developed as was done in arriving at equation (9), *i.e.*

$$\frac{d\Sigma_s}{d\Omega} = \frac{\langle b\rangle^2}{V}\left|\sum_i^{N_m}\exp(i\mathbf{Q}\cdot\mathbf{r}_i)\right|^2 + \frac{\varphi_{H_2O}\varphi_{D_2O}}{v_m}\left(\langle b_{H_2O}\rangle - \langle b_{D_2O}\rangle\right)^2$$

$$+ \frac{\varphi_{H_2O}}{v_m}\left(\langle b_{H_2O}^2\rangle - \langle b_{H_2O}\rangle^2\right) + \frac{\varphi_{D_2O}}{v_m}\left(\langle b_{D_2O}^2\rangle - \langle b_{D_2O}\rangle^2\right), \quad (26)$$

where v_m is the volume of one molecule, and φ_{H_2O} (φ_{D_2O}) is the volume fraction of H_2O (D_2O). Equation (26) shows explicitly that the flat 'background' seen at low Q from such mixtures consists of a combination of diffuse coherent scattering (second term) and true incoherent scattering (third and fourth terms).

From the scattering lengths and cross sections tabulated by Sears (1992),

$$\langle b_{H_2O}\rangle = 2\langle b_H\rangle + \langle b_O\rangle$$
$$= 2(-3.74\ \text{fm}) + 5.80\ \text{fm} = -1.68\ \text{fm}, \quad (27)$$

$$\langle b_{D_2O}\rangle = 2\langle b_D\rangle + \langle b_O\rangle$$
$$= 2(6.67\ \text{fm}) + 5.80\ \text{fm} = 19.14\ \text{fm}, \quad (28)$$

$$\langle b_{H_2O}^2\rangle = \left\langle \left(b_{H_1} + b_{H_2} + b_O\right)^2 \right\rangle$$
$$= 2\langle b_H^2\rangle + \langle b_O^2\rangle + 4\langle b_H\rangle\langle b_O\rangle + 2\langle b_H\rangle^2$$
$$= 2(6.53\ \text{barns}) + (0.337\ \text{barns})$$
$$+ 4(-3.74\ \text{fm})(5.80\ \text{fm}) + 2(-3.74\ \text{fm})^2$$
$$= 12.81\ \text{barns}, \quad (29)$$

$$\langle b_{D_2O}^2\rangle = \left\langle \left(b_{D_1} + b_{D_2} + b_O\right)^2 \right\rangle$$
$$= 2\langle b_D^2\rangle + \langle b_O^2\rangle + 4\langle b_D\rangle\langle b_O\rangle + 2\langle b_D\rangle^2$$
$$= 2(0.608\ \text{barns}) + (0.337\ \text{barns}) \quad (30)$$
$$+ 4(6.67\ \text{fm})(5.80\ \text{fm}) + 2(6.67\ \text{fm})^2$$
$$= 3.99\ \text{barns}.$$

Hence, equation (26) becomes

$$\frac{d\Sigma_s}{d\Omega} = \frac{\langle b\rangle^2}{V}\left|\sum_i^{N_m}\exp(i\mathbf{Q}\cdot\mathbf{r}_i)\right|^2$$

$$+ \frac{\varphi_{H_2O}\varphi_{D_2O}}{v_m}(-1.68\ \text{fm} - 19.14\ \text{fm})^2$$

$$+ \frac{\varphi_{H_2O}}{v_m}(12.81\ \text{barns} - 0.028\ \text{barns})$$

$$+ \frac{\varphi_{D_2O}}{v_m}(3.99\ \text{barns} - 3.66\ \text{barns}) \quad (31)$$

or, in terms of the total cross section per molecule,

$$\sigma_s = \left\{ \frac{4\pi\langle b\rangle^2}{N_m}\int\left|\sum_i^{N_m}\exp(i\mathbf{Q}\cdot\mathbf{r}_i)\right|^2 d\Omega + \varphi_{H_2O}\varphi_{D_2O}\,54.47\ \text{barns} \right.$$

$$\left. + \varphi_{H_2O}\,160.60\ \text{barns} + \varphi_{D_2O}\,4.15\ \text{barns} \right\}. \quad (32)$$

Notice that equation (26) is the basis for the high-concentration labeling technique used to study the conformation of polymer chains in mixtures of protonated and perdeuterated chains in the melt (Akcasu *et al.*, 1980). Equation (26) can be extended to larger molecules by including the molecular form factor in the second term, which is another demonstration that this term represents coherent, not incoherent, scattering.

2.4. H_2O/D_2O mixtures (including H/D exchange)

For water there is exchange of H and D. For this reason, the second (coherent scattering) term in equation (26) is reduced in real water, as pointed out by Arleth & Pedersen (2000). To show this explicitly we begin again from equation (20):

$$\frac{d\Sigma_s}{d\Omega} = \frac{1}{V}\left\langle \left|\sum_i^{N_m} b_i \exp(i\mathbf{Q}\cdot\mathbf{r}_i)\right|^2 \right\rangle$$

$$= \frac{1}{V}\langle b\rangle^2\left|\sum_i^{N_m}\exp(i\mathbf{Q}\cdot\mathbf{r}_i)\right|^2 + \frac{N_m}{V}\left(\langle b^2\rangle - \langle b\rangle^2\right). \quad (33)$$

In this case we have three types of molecules to consider: H_2O, D_2O, and HDO or DHO (HDO and DHO are indistinguishable in terms of their scattering lengths, hence there are three and not four types of molecules to consider). Hence

$$\langle b\rangle = f_{H_2O}\langle b_{H_2O}\rangle + f_{D_2O}\langle b_{D_2O}\rangle + f_{HDO}\langle b_{HDO}\rangle$$
$$\text{with } f_{H_2O} + f_{D_2O} + f_{HDO} = 1, \quad (34)$$

where f_{H_2O}, f_{D_2O} and f_{HDO} are the fractions of H_2O, D_2O and HDO (or DHO) molecules in the mixture, respectively.

The number of H atoms in the mixture is $N_H = 2\varphi_{H_2O}N_m$, where N_m is the number of molecules and φ_{H_2O} is the volume fraction of H_2O that is mixed with a volume fraction $(1 - \varphi_{H_2O})$ of D_2O. Similarly $N_D = 2(1 - \varphi_{H_2O})N_m$. Hence when the mixture is at chemical equilibrium,

$$f_{H_2O} = \left(\frac{N_H}{2N_m}\right)^2 = \left(\frac{2\varphi_{H_2O}N_m}{2N_m}\right)^2 = \varphi_{H_2O}^2,$$

$$f_{D_2O} = \left(\frac{N_D}{2N_m}\right)^2 = \left[\frac{2(1-\varphi_{H_2O})N_m}{2N_m}\right]^2 = (1-\varphi_{H_2O})^2, \quad (35)$$

$$f_{HDO} = \left[\frac{N_H N_D}{(2N_m)^2}\right] = 2\,\varphi_{H_2O}(1-\varphi_{H_2O}).$$

Thus,

$$\langle b \rangle = \varphi_{H_2O}^2 \langle b_{H_2O}\rangle + (1-\varphi_{H_2O})^2 \langle b_{D_2O}\rangle \\ + 2\varphi_{H_2O}(1-\varphi_{H_2O})\langle b_{HDO}\rangle. \quad (36)$$

Similarly,

$$\langle b^2 \rangle = \varphi_{H_2O}^2 \langle b_{H_2O}^2\rangle + (1-\varphi_{H_2O})^2 \langle b_{D_2O}^2\rangle \\ + 2\varphi_{H_2O}(1-\varphi_{H_2O})\langle b_{HDO}^2\rangle. \quad (37)$$

The terms $\langle b_{H_2O}^2 \rangle$ and $\langle b_{D_2O}^2 \rangle$ are given in equations (30) and (31), respectively; and

$$\langle b_{HDO}^2 \rangle = \langle (b_H + b_D + b_O)^2 \rangle = \langle b_H^2 \rangle + \langle b_D^2 \rangle + \langle b_O^2 \rangle \\ + 2\langle b_H\rangle\langle b_D\rangle + 2\langle b_H\rangle\langle b_O\rangle + 2\langle b_D\rangle\langle b_O\rangle. \quad (38)$$

Substituting equations (36), (37) and (38) into (33) gives, after some manipulation,

$$\frac{d\Sigma_s}{d\Omega} = \frac{\langle b\rangle^2}{V}\left|\sum_i^{N_m} \exp(i\mathbf{Q}\cdot\mathbf{r}_i)\right|^2 + \frac{\varphi_{H_2O}}{v_m}\left(\langle b_{H_2O}^2\rangle - \langle b_{H_2O}\rangle^2\right) \\ + \frac{(1-\varphi_{H_2O})}{v_m}\left(\langle b_{D_2O}^2\rangle - \langle b_{D_2O}\rangle^2\right) \\ + \frac{2\varphi_{H_2O}(1-\varphi_{H_2O})}{v_m}\left(\langle b_H\rangle - \langle b_D\rangle\right)^2. \quad (39)$$

For comparison, equation (26) can be written as

$$\frac{d\Sigma_s}{d\Omega} = \frac{\langle b\rangle^2}{V}\left|\sum_i^{N_m} \exp(i\mathbf{Q}\cdot\mathbf{r}_i)\right|^2 + \frac{\varphi_{H_2O}}{v_m}\left(\langle b_{H_2O}^2\rangle - \langle b_{H_2O}\rangle^2\right) \\ + \frac{(1-\varphi_{H_2O})}{v_m}\left(\langle b_{D_2O}^2\rangle - \langle b_{D_2O}\rangle^2\right) \\ + \frac{4\varphi_{H_2O}(1-\varphi_{H_2O})}{v_m}\left(\langle b_H\rangle - \langle b_D\rangle\right)^2. \quad (40)$$

The only difference between equations (39) and (40) is in the diffuse coherent scattering term (the last term in each), which is reduced by a factor of two when H/D exchange is included. It is instructive to note that the 'true' incoherent scattering terms in both (40) and (39) are the same, as they must be since this scattering does not depend on where the atoms are located.

The coherent [fourth term in (39) and (40)] and incoherent [second and third terms in equations (39) and (40)] contributions to the total low-Q scattering from H_2O/D_2O mixtures are plotted in Fig. 2.

The reduction in the diffuse coherent scattering when H/D exchange is included in the calculation begs the question, where does the diffuse scattering go? To understand this, we compare the Q-dependent coherent scattering terms in equations (39) and (40), which are proportional to $\langle b \rangle^2$:

$$\langle b\rangle^2_{wo} = \left[\varphi_{H_2O}\langle b_{H_2O}\rangle + (1-\varphi_{H_2O})\langle b_{D_2O}\rangle\right]^2 \quad (41)$$

without H/D exchange, and

$$\langle b\rangle^2_{w} = \left[\varphi_{H_2O}^2\langle b_{H_2O}\rangle + (1-\varphi_{H_2O})^2\langle b_{D_2O}\rangle \\ + 2\varphi_{H_2O}(1-\varphi_{H_2O})\langle b_{HDO}\rangle\right]^2 \quad (42)$$

with H/D exchange. Then

$$\langle b\rangle^2_{w} - \langle b\rangle^2_{wo} = \left(\langle b_w\rangle - \langle b_{wo}\rangle\right)\left(\langle b_w\rangle + \langle b_{wo}\rangle\right) \quad (43)$$

and

$$\langle b_w\rangle - \langle b_{wo}\rangle = \left[\varphi_{H_2O}^2\langle b_{H_2O}\rangle + (1-\varphi_{H_2O})^2\langle b_{D_2O}\rangle \\ + 2\varphi_{H_2O}(1-\varphi_{H_2O})\langle b_{HDO}\rangle\right] \\ - \left[\varphi_{H_2O}\langle b_{H_2O}\rangle + (1-\varphi_{H_2O})\langle b_{D_2O}\rangle\right] \\ = \varphi_{H_2O}(1-\varphi_{H_2O})\left(2\langle b_{HDO}\rangle - \langle b_{H_2O}\rangle - \langle b_{D_2O}\rangle\right) \\ = 0. \quad (44)$$

Hence the reduction in the diffuse coherent scattering due to H/D exchange is not accompanied by a corresponding increase in the intermolecular Q-dependent coherent scattering. The reduction in diffuse coherent scattering therefore likely appears (although not shown here) in the intramolecular coherent scattering (at larger Q), which we have neglected in this treatment.
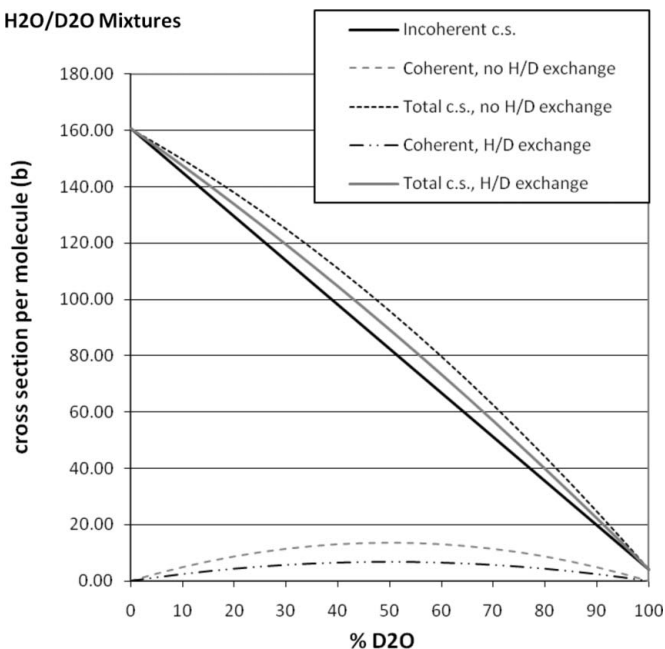

Figure 2
The calculated coherent, incoherent and total (sum of coherent and incoherent) cross sections per molecule from mixtures of H_2O and D_2O. The coherent scattering is calculated for both the case where exchange of hydrogen and deuterium between molecules is allowed, as in real water, and when there is no exchange.

3. Demonstration experiment

To demonstrate the distinction between diffuse coherent scattering and true incoherent scattering, we have measured the small-angle neutron scattering (SANS) from titanium dioxide, TiO_2. This molecular material was chosen because titanium is one of only a few elements with a negative coherent scattering length. In addition the isotopic and nuclear spin incoherent scattering for both oxygen and titanium are small compared to most elements. As a result, if there were a diffuse scattering term [the middle term in equation (9)] in the cross section, it would dominate the measured SANS and be easily identified by putting the scattering on an absolute scale. However, for such a term to exist in the cross section for TiO_2, the positions of the titanium and oxygen atoms must be completely uncorrelated, which is physically not the case.

From equation (18) the incoherent macroscopic cross section for TiO_2 is

$$\Sigma_{incoh,TiO_2} = \sum_j^N n_j \sigma_{incoh,j} = n_{Ti}\sigma_{incoh,Ti} + n_O\sigma_{incoh,O}. \quad (45)$$

From the mass density ($\rho = 4.23$ g cm^{-3}) and molecular weight (79.9 atomic mass units) of TiO_2, the atomic number densities are $n_{Ti} = 3.19 \times 10^{22}$ cm^{-3} and $n_O = 2n_{Ti}$. The elemental incoherent cross sections are (Sears, 1992) $\sigma_{incoh,Ti} = 2.87$ barns and $\sigma_{incoh,O} \simeq 0$ barns. Hence

$$\Sigma_{incoh,TiO_2} = 0.092 \text{ cm}^{-1}. \quad (46)$$

The additional Q-independent scattering that would arise if the Ti and O atoms were completely disordered is given by the second term of equation (9), which we call $\Sigma_{c,Laue}$ as in the NaCl example:

$$\Sigma_{c,Laue} = 4\pi\frac{d\Sigma_{c,Laue}}{d\Omega} = 4\pi\frac{N}{V}\frac{1}{2}\sum_{\substack{i,j \\ i\neq j}}^m f_i f_j \left(\langle b_i\rangle - \langle b_j\rangle\right)^2,$$
$$\Sigma_{c,Laue} = 4\pi\left(3\,n_{Ti}\right)\frac{1}{3}\frac{2}{3}\left(\langle b_{Ti}\rangle - \langle b_O\rangle\right)^2 = 0.28 \text{ cm}^{-1}, \quad (47)$$

where $\langle b_{Ti}\rangle = b_{c,Ti} = -3.44$ fm and $\langle b_O\rangle = b_{c,O} = 5.80$ fm (Sears, 1992). The disordered scattering term is three times larger than the true incoherent scattering and hence should be readily apparent from the scale of the Q-independent SANS.

For the SANS, measurements a 2 mm-path-length quartz cell was filled with a coarse TiO_2 powder. The cell was weighed before and after filling to estimate the bulk density of the powder in the cell. This was found to be 0.99 g cm^{-3}. Hence the cross sections per unit volume given in equations (46) and (47) should be multiplied by 0.99/4.23 for comparison with the scattering from this particular sample. The measurements were made on the 30 m SANS instrument on neutron guide NG-7 at NIST using a wavelength of 6 Å and a sample-to-detector distance of 1 m. The particle size of tens of micrometres does produce SANS at very low Q, which decays roughly as Q^{-4}. At larger Q, still in the SANS region, the scattering becomes essentially flat at a level that was put on an absolute scale by measuring the neutrons per second incident

on the sample. In addition to the scattering from the sample in its cell, scattering from the empty cell was also measured and subtracted taking into account room background and the transmission of the sample. The resulting SANS for the TiO_2 is shown in Fig. 3 along with the scattering from a reference sample of D_2O treated in the same way. The Q-independent scattering is slightly lower, perhaps as a result of over-estimating the bulk density of the sample, than the calculated level of incoherent scattering but far below the level expected from the sum of incoherent plus disordered coherent scattering.

4. Discussion

The incoherent scattering discussed here, which arises solely from the lack of any correlation between an atom's location and that atom's nuclear spin state or nuclear isotope, is unique to neutron scattering. There is no analog in X-ray scattering. Scattering that arises from atomic disorder, such a Laue monotonic scattering (Warren, 1969), is present in both X-ray and neutron scattering. Because atomic disorder scattering may be nearly Q independent, like the incoherent scattering, authors of neutron scattering papers and texts have in some cases referred to this scattering as compositional or mixture incoherent scattering. However, this designation blurs the distinction between true incoherent scattering, which has no
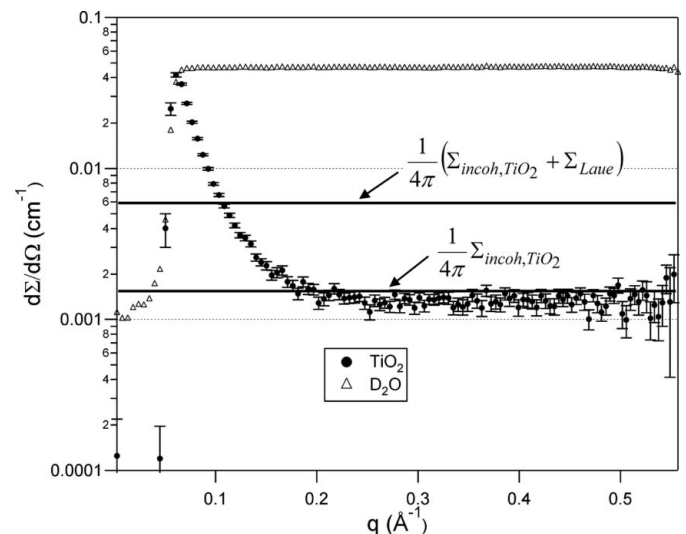
Figure 3
The measured SANS from a powder sample of TiO_2 with a bulk density of -0.99 g cm^{-3}. The rise at low Q is due to scattering from the surfaces of the particles in the powder. The flat scattering from 0.2 to 0.5 Å^{-1} is consistent with the calculated incoherent scattering for this sample [from equation (46) after scaling by the ratio of the bulk density to the theoretical density], but is far below the level calculated by including the disorder scattering term in equation (47). These data clearly demonstrate the absence of any so-called 'compositional incoherent' scattering. The error bars in the figure represent one standard deviation. Also included for reference is the scattering measured from a 2 mm-thick sample of D_2O under the same conditions and treated the same way, which gave the expected value of $d\Sigma_s/d\Omega \simeq 0.05$ cm^{-1}. [The incoherent contribution to the low-Q scattering from D_2O is, from the last term of equation (31), only 0.011 cm^{-1}. Most of the scattering is coherent, and from the cross section per molecule at $\lambda = 6$ Å, $\sigma_s = 22$ barns (BNL 325), the total cross section per unit volume is $d\Sigma_s/d\omega = 0.059$ cm^{-1}.]

structural information, and what is more properly referred to as diffuse coherent scattering, which does contain structural information pertaining to the degree of atomic disorder.

The salient point is that incoherent cross sections are simply additive. Hence the macroscopic incoherent scattering cross section for a material is readily calculated from

$$\Sigma_{\mathrm{incoh}} = \sum_{j}^{N} n_j \sigma_{\mathrm{incoh},j}, \tag{48}$$

where N is the number of atomic species in the material, n_j is the number density of atomic species j and $\sigma_{\mathrm{incoh},j}$ is the tabulated incoherent scattering cross section for element j. For any material with an appreciable amount of hydrogen, a good approximation for the bulk incoherent cross section is simply, $\Sigma_{\mathrm{incoh}} \simeq n_{\mathrm{H}}\sigma_{\mathrm{incoh,H}}$, since the incoherent cross section for hydrogen is so much larger than that for other elements.

Caveat. The coherent and incoherent cross sections tabulated by Sears (1992) are calculated from the bound scattering lengths for nuclei. The actual cross sections depend on the incoming neutron energy and sample temperature, especially for light elements. For cold neutrons, the tabulated cross sections are generally a lower limit. The measured incoherent scattering from hydrogen, for example, can be considerably larger than its bound value. For example,

$$\Sigma_{\mathrm{incoh}}(H_2O) = 5.37 \text{ cm}^{-1} \tag{49}$$

[from tables of scattering lengths given by Sears (1992)] and

$$\Sigma_{\mathrm{T}}(H_2O) \cong 7.7 \text{ cm}^{-1} \tag{50}$$

[measured for 1 meV, or 0.9 nm, neutrons at 290 K (BNL 325)].

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