Partial Structure Factors in Multicomponent Liquid or Amorphous Alloys

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The structure of a ν component liquid or amorphous alloy is analyzed in terms of $\nu(\nu+1)/2$ independent partial structure factors which are associated to the different correlations between the numbers of particles of all chemical species. This formalism, which is specially adapted to the study of alloys of more than two components, is related to Fournet-Faber-Ziman and extended Bhatia-Thornton theory. Sum rules, inequality relations and limiting values are calculated in the static approximation and Debye pair expressions of the structure factors are derived in the isotropic approximation.

1. Introduction

Fournet, Faber and Ziman[1–3] first analyzed the structure of a ν component liquid alloy in terms of $\nu(\nu+1)/2$ independent partial interference functions. In order to relate the values of the cross-section at small scattering angles to thermodynamical fluctuations, Bhatia and Thornton[4] introduced a new formalism which describes the different correlations between the concentrations and the total number of particles in a binary system.

In this paper we define a set of $\nu(\nu+1)/2$ independent structure factors which characterize the correlations between the number of particles of all chemical species and we extend Bhatia and Thornton's theory to multicomponent systems. We then relate the three precedent formalisms and calculate sum rules, inequality relations and limiting values of the cross-sections in the static approximation. Pair expressions of the partial structure factors are finally derived in the isotropic approximation.

2. Van Hove's Formalism

Let us consider a scattering experiment where a beam of particles with mass m and wave vector $\boldsymbol{k}_0$ $(k_0 = 2\pi/\lambda)$ is scattered by a liquid or amorphous alloy at an angle 2Θ with a wave vector $\boldsymbol{k}$ corresponding to a momentum transfer $\hbar\varkappa = \hbar(\boldsymbol{k}_0 - \boldsymbol{k})$ and to an energy transfer

$$\varepsilon = \hbar\,\omega = \frac{\hbar^2}{2\,m}\,(k_0{}^2 - k^2)$$

Each of the ν chemical species α of the system is characterized by its mean relative concentration $\bar{c}_\alpha = \bar{N}_\alpha/\bar{N}$ or its mean number density $\bar{n}_\alpha = \bar{N}_\alpha/V$ where $\bar{N} = \Sigma\,\bar{N}_\alpha$ is the mean total number of particles in the irradiated * volume V.

The differential scattering cross-section per scattering centre, unit solid angle and unit energy transfer is given by Van Hove's formula[5]:

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\,\mathrm{d}\varepsilon} = \frac{k}{k_0}\,\frac{1}{N}\,\frac{1}{2\,\pi\,\hbar}\int e^{-i\omega t}\,\mathrm{d}t\left\langle \sum_{i\alpha j\beta}\frac{m^2}{4\,\pi^2\,\hbar^4}\,W_{i\alpha}(\boldsymbol{\varkappa})\,W_{j\beta}{}^*(\boldsymbol{\varkappa})\,\langle\exp\{-i\,\boldsymbol{\varkappa}\,\boldsymbol{R}_j{}^\beta(o)\}\exp\{i\,\boldsymbol{\varkappa}\,\boldsymbol{R}_i{}^\alpha(t)\}\rangle\right\rangle_{\mathrm{I}} \tag{1}$$

where each particle i, α is characterized by its time dependent position operator $\boldsymbol{R}_i{}^\alpha(t)$ and by the Fourier transform of its potential energy interaction with the incident particles

$$W_{i\alpha}(\boldsymbol{\varkappa}) = \int e^{i\boldsymbol{\varkappa}\boldsymbol{r}}\,V_{i\alpha}(\boldsymbol{r})\,\mathrm{d}_3 r\,.$$

In the case of nuclear scattering of slow neutrons, the expression

$$(m^2/4\,\pi^2\,\hbar^4)\,W_{i\alpha}(\boldsymbol{\varkappa})\,W_{j\beta}{}^*(\boldsymbol{\varkappa})$$

is equal to the product of the Fermi scattering lengths $b_{i\alpha}\,b_{j\beta}$ and is independent of $\boldsymbol{\varkappa}$, whereas for unpolarized X-ray scattering this quantity has to be replaced by

$$r_\mathrm{e}{}^2\,\tfrac{1}{2}(1+\cos^2 2\,\Theta)\,f_\alpha(\varkappa)\,f_\beta(\varkappa)$$

$r_\mathrm{e} = e^2/m\,c^2$ being the classical electron radius and $f_\alpha(\varkappa)$ the $\varkappa$ dependent atomic scattering factor which is equal to the atomic number Z_α at $\varkappa = 0$. In for-

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* The irradiated volume is supposed to be smaller than the sample volume.

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mula (1) the internal brackets $\langle\ \rangle$ stand for the thermal average over the target states and the external brackets $\langle\ \rangle_I$, which are only necessary in the neutron scattering case, represent the average over all neutron spin states, isotopes and nuclear spin distributions.

From this point, for the sake of brevity, we shall only develop the formulae appropriate to nuclear scattering of slow neutrons.

Cross-section (1) is usually split[5] into an incoherent * and a coherent scattering cross-section:

$$\left(\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\,\mathrm{d}\varepsilon}\right)_{\mathrm{Inc}} = \frac{k}{k_0}\sum_{\alpha} b^2_{\mathrm{Inc}\,\alpha}\frac{1}{N}\frac{1}{2\pi\hbar} \tag{2}$$

$$\int e^{-i\omega t}\,\mathrm{d}t\,\langle\sum_i \exp\{-i\,\varkappa\,\mathbf{R}_i^{\alpha}(o)\}\exp\{i\,\varkappa\,\mathbf{R}_i^{\alpha}(t)\}\rangle$$

where

$$b^2_{\mathrm{Inc}\,\alpha} = \langle b^2_{i\alpha}\rangle_{\mathrm{I}} - \langle b_{i\alpha}\rangle_{\mathrm{I}}^2$$

is the incoherent cross-section of element α, and

$$\left(\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\,\mathrm{d}\varepsilon}\right)_{\mathrm{Coh}} = \frac{k}{k_0}\sum_{\alpha\beta} b_{\mathrm{Coh}\,\alpha}\,b_{\mathrm{Coh}\,\beta}\frac{1}{N}\frac{1}{2\pi\hbar} \tag{3}$$

$$\int e^{-i\omega t}\,\mathrm{d}t\sum_{ij}\langle\exp\{-i\,\varkappa\,\mathbf{R}_j^{\beta}(o)\}\exp\{i\,\varkappa\,\mathbf{R}_i^{\alpha}(t)\}\rangle$$

where $b_{\mathrm{Coh}\,\alpha} = \langle b_{i\alpha}\rangle_I$ is the coherent scattering length of element α. The coherent cross-section may also be written in a more compact way as

$$\left(\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\,\mathrm{d}\varepsilon}\right)_{\mathrm{Coh}} = \frac{k}{k_0}\frac{1}{N}\frac{1}{2\pi\hbar}$$

$$\int e^{-i\omega t}\,\mathrm{d}t\langle A^{+}(\varkappa,0)\,A(\varkappa,t)\rangle$$

where

$$A(\varkappa,t) = \sum_{\alpha} b_{\mathrm{Coh}\,\alpha}\sum_i \exp\{i\,\varkappa\,\mathbf{R}_i^{\alpha}(t)\} \tag{4}$$

is the scattering amplitude operator.

3. Partial Number Structure Factors and Generalized Bhatia Thornton Formalism

Following Bhatia and Thornton[4], we first introduce the local deviation operators in the partial and total number of particles in the volume V:

$$\delta N_{\alpha}(\boldsymbol{r},t) = F(\boldsymbol{r})\,[V\sum_i \delta[\mathbf{r} - \mathbf{R}_i^{\alpha}(t)] - N_{\alpha}]$$

(δ stands for the Dirac distribution and $F(\boldsymbol{r})$ is the geometrical form factor which is equal to unity within total number of particles in the volume V:

$$\delta N(\boldsymbol{r},t) = \sum_{\alpha}\delta N_{\alpha}(\boldsymbol{r},t)$$

and their Fourier transforms

$$N_{\alpha}(\varkappa,t) = \frac{1}{V}\int e^{i\varkappa\boldsymbol{r}}\,\delta N_{\alpha}(\boldsymbol{r},t)\,\mathrm{d}_3 r = \sum_{i=1}^{N_{\alpha}}\exp\{i\,\varkappa\,\mathbf{R}_i^{\alpha}(t)\} - \overline{N}_{\alpha}\,\Phi(\varkappa)$$

$$N(\varkappa,t) = \sum_{\alpha} N_{\alpha}(\varkappa,t) = \sum_{i\alpha}\exp\{i\,\varkappa\,\mathbf{R}_i^{\alpha}(t)\} - \overline{N}\,\Phi(\varkappa)$$

where:

$$\Phi(\varkappa) = \frac{1}{V}\int e^{i\varkappa r}F(\mathbf{r})\,\mathrm{d}_3 r$$

is the fourier transform of the form factor whose modulus is negligible with respect to 1 except near $\varkappa = 0$ where it tends to 1.

We also define the local deviation operators in the concentrations:

$$\delta c_{\alpha}(\boldsymbol{r},t) = \frac{1}{N}\,[\delta N_{\alpha}(\boldsymbol{r},t) - \overline{c}_{\alpha}\,\delta N(\boldsymbol{r},t)]$$

and their Fourier transform:

$$C_{\alpha}(\varkappa,t) = \frac{1}{N}\,[N_{\alpha}(\varkappa,t) - \overline{c}_{\alpha}\,N(\varkappa,t)]$$

$$= \frac{1}{N}\left[\sum_i \exp\{i\,\varkappa\,\mathbf{R}_i^{\alpha}(t)\} - \overline{c}_{\alpha}\sum_{j\beta}\exp\{i\,\varkappa\,\mathbf{R}_j^{\beta}(t)\}\right].$$

We are then able to introduce a first set of $\nu(\nu+1)/2$ independent 'partial number structure factor' $\mathcal{N}_{\alpha\beta}{}^{4}\varkappa,\omega)$ which are associated to the correlations between partial numbers N_{α} and N_{β}:

$$\mathcal{N}_{\alpha\beta}(\varkappa,\omega) = \frac{1}{N}\frac{1}{2\pi\hbar} \tag{5}$$

$$\int e^{-i\omega t}\,\mathrm{d}t\tfrac{1}{2}\,\langle N_{\alpha}^{+}(\varkappa,o)\,N_{\beta}(\varkappa,t) + N_{\beta}^{+}(\varkappa,o)\,N_{\alpha}(\varkappa,t)\rangle$$

(with $\mathcal{N}_{\alpha\beta} = \mathcal{N}_{\beta\alpha}$).

Using this formalism, one obtains an expression of the coherent cross-section:

$$\left(\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\,\mathrm{d}\varepsilon}\right)_{\mathrm{Coh}} = \frac{k}{k_0}\sum_{\alpha\beta} b_{\mathrm{Coh}\,\alpha}\,b_{\mathrm{Coh}\,\beta}\,\mathcal{N}_{\alpha\beta}(\varkappa,\omega) \tag{6}$$

which is valid except near $\varkappa = 0$ because the terms containing $\Phi(\varkappa)$ must then be dropped in the structure factor expressions. The diagonal terms

$$(k/k_0)\,b^2_{\mathrm{Coh}\,\alpha}\,\mathcal{N}_{\alpha\alpha}(\varkappa,\omega)$$

involved in this equation represent the coherent cross-sections of partial liquids α.

We also define a second set of generalized Bhatia-Thornton structure factors which are associated with the different time dependent correlations between the total number of particles and the concentrations:

$$S_{NN}(\varkappa,\omega) = \frac{1}{N}\frac{1}{2\pi\hbar}\int e^{-i\omega t}\,\mathrm{d}t\langle N^{+}(\varkappa,o)\,N(\varkappa,t)\rangle\,, \tag{7}$$

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* This incoherent scattering cross-section vanishes in the X-ray scattering case.

$$S_{Nc_\alpha}(\varkappa, \omega) = \frac{1}{2\pi\hbar} \int e^{-i\omega t}\, \mathrm{d}t\, \tfrac{1}{2} \langle N^+(\varkappa, o)\, C_\alpha(\varkappa, t) + C_\alpha{}^+(\varkappa, o)\, N(\varkappa, t) \rangle\,, \tag{8}$$

$$S_{c_\alpha c_\beta}(\varkappa, \omega) = \frac{\overline{N}}{2\pi\hbar} \int e^{-i\omega t}\, \mathrm{d}t\, \tfrac{1}{2} \langle C_\alpha{}^+(\varkappa, o)\, C_\beta(\varkappa, t) + C_\beta{}^+(\varkappa, o)\, C_\alpha(\varkappa, t) \rangle \tag{9}$$

(with $S_{c_\alpha c_\beta} = S_{c_\alpha c_\beta}$) ,

and obey the sum rules

$$\sum_\alpha S_{Nc\alpha} = 0\,, \quad \sum_\beta S_{c_\alpha c_\beta} = 0\,. \tag{10}$$

Using the expression of the scattering amplitude operator

$$A(\varkappa, t) = b_{\mathrm{Coh}}\, N(\varkappa, t) + \overline{N} \sum_\alpha b_{\mathrm{Coh}\,\alpha}\, C_\alpha(\varkappa, t)$$

where

$$b_{\mathrm{Coh}} = \sum_\alpha \overline{c}_\alpha\, b_{\mathrm{Coh}\,\alpha}\,. \tag{11}$$

is the mean coherent scattering length averaged over all chemical elements, it is easy to express the coherent cross-section by means of these $\nu(\nu+1)/2$ independent structure factors:

$$\left(\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\, \mathrm{d}\varepsilon}\right)_{\mathrm{Coh}} = \frac{k}{k_0} [b^2_{\mathrm{Coh}}\, S_{NN}(\varkappa, \omega) + 2\, b_{\mathrm{Coh}} \sum_\alpha b_{\mathrm{Coh}\,\alpha}\, S_{Nc\alpha}(\varkappa, \omega) - \tfrac{1}{2} \sum_{\alpha\beta} (b_{\mathrm{Coh}\,\alpha} - b_{\mathrm{Coh}\,\beta})^2\, Sc_\alpha c_\beta(\varkappa, \omega)]\,. \tag{12}$$

This expression is again valid except near $\varkappa = 0$.

Equation (12) only involves the non-diagonal terms $S\, c_\alpha\, c_\beta$, which describe the correlations between different concentrations. However, in the special case of binary alloys, the coherent cross-section may be expressed with the aid of the diagonal term $S\, c_1\, c_1$ since according to relation (10): $S\, c_1\, c_2 = - S\, c_1\, c_1$. It is for this reason that Bhatia and Thornton's theory is simple and useful in binary alloy studies.

Finally, from the two expressions of the cross-section (6) and (12), and identifying the coefficients of $b_{\mathrm{Coh}\,\alpha}\, b_{\mathrm{Coh}\,\beta}$, one easily shows the relations between partial number and Bhatia Thornton structure factors *:

$$\mathcal{N}_{\alpha\beta} = c_\alpha\, c_\beta\, S_{NN} + c_\alpha\, S_{Nc_\beta} + c_\beta\, S_{Nc\alpha} + Sc_\alpha c_\beta\,, \tag{13}$$

$$S_{NN} = \sum_{\gamma\delta} \mathcal{N}_{\gamma\delta}\,, \tag{14}$$

$$S_{Nc\alpha} = \sum_\gamma \mathcal{N}_{\alpha\gamma} - c_\alpha \sum_{\gamma\delta} \mathcal{N}_{\gamma\delta}\,, \tag{15}$$

$$Sc_\alpha c_\beta = \mathcal{N}_{\alpha\beta} - \sum_\gamma [c_\alpha\, \mathcal{N}_{\beta\gamma} + c_\beta\, \mathcal{N}_{\alpha\gamma}] + c_\alpha\, c_\beta \sum_{\gamma\delta} \mathcal{N}_{\gamma\delta}\,. \tag{16}$$

4. Static Approximation and Fournet-Faber-Ziman Formalism

In the remaining part of this paper we shall deal only with the static approximation where the energy of the incident particles is assumed to be large with respect to the energy interchanges with the target and the double differential cross-sections are easily integrated over the energies [5]. In these conditions and making use of the relations

$$\frac{1}{2\pi} \int e^{i\omega t}\, \mathrm{d}\omega = \delta(t) \quad \text{and} \quad \frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \int \frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\, \mathrm{d}\varepsilon}\, \mathrm{d}\varepsilon$$

one obtains the expression of the incoherent cross-section:

$$(\mathrm{d}\sigma/\mathrm{d}\Omega)_{\mathrm{Inc}} = \sum_\alpha c_\alpha\, b^2_{\mathrm{Inc}\,\alpha} \tag{17}$$

and a first form of the coherent cross-section:

$$(\mathrm{d}\sigma/\mathrm{d}\Omega)_{\mathrm{Coh}} = \sum_{\alpha\beta} b_{\mathrm{Coh}\,\alpha}\, b_{\mathrm{Coh}\,\beta}\, \mathcal{N}_{\alpha\beta}(\varkappa) \tag{18}$$

where the partial number structure factors are equal to

$$\mathcal{N}_{\alpha\beta}(\varkappa) = \frac{1}{\overline{N}} [\langle \tfrac{1}{2}(\sum_{ij} \exp\{i\, \varkappa (\mathbf{R}_i{}^\alpha - \mathbf{R}_j{}^\beta)\} + C\, C) \rangle - \overline{N}_\alpha\, \overline{N}_\beta |\, \Phi(\varkappa)\, |^2]^{**}\,. \tag{19}$$

In this equation $\boldsymbol{R}_i{}^\alpha$ and $\boldsymbol{R}_j{}^\beta$ refer to the same time and need not be considered as quantum operators and $\varkappa = 4\,\pi(\sin\Theta)/\lambda$. When $\varkappa$ tends to infinity, the partial number structure factors $\mathcal{N}_{\alpha\beta}(\varkappa)$ tend to $c_\alpha\, \delta_{\alpha\beta}$ where $\delta_{\alpha\beta}$ is the Kronecker symbol.

In the same way, the generalized Bhatia Thornton expression of the coherent cross-section, is given by

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_{\mathrm{Coh}} = b^2_{\mathrm{Coh}}\, S_{NN}(\varkappa) + 2\, b_{\mathrm{Coh}} \sum_\alpha b_{\mathrm{Coh}\,\alpha}\, S_{Nc\alpha}(\varkappa) - \tfrac{1}{2} \sum_{\alpha\beta} (b_{\mathrm{Coh}\,\alpha} - b_{\mathrm{Coh}\,\beta})^2\, S_{c_\alpha c_\beta}(\varkappa) \tag{20}$$

or

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_{\mathrm{Coh}} = \left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_{NN} + \left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_{Nc} + \left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_{\mathrm{cc}}$$

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* We drop the bars on c_α, c_β, N_α and N when they are not necessary.

** cc means complex conjugate.

with

$$S_{NN}(\varkappa) = \frac{1}{N}\,[\langle \sum_{i\alpha j\beta} \exp\{i\,\varkappa(\mathbf{R}_i^{\alpha} - \mathbf{R}_j^{\beta})\}\rangle - \bar{N}^2\,|\,\Phi(\varkappa)\,|^2]^{*}. \tag{21}$$

$(\mathrm{d}\sigma/\mathrm{d}\Omega)_{NN}$ is the truly coherent cross-section since it is proportional to the mean Fermi scattering length averaged over all chemical elements, isotopes and nuclear spin distributions and to a geometrical structure factor $S_{NN}(\varkappa)$ (going to 1 when $\varkappa$ goes to infinity) involving all atomic positions.

$(\mathrm{d}\sigma/\mathrm{d}\Omega)_{Nc}$ describes the correlations between the total number of scattering centres and the different concentrations. Each term $S_{Nc_\alpha}(\varkappa)$ tends to 0 as $\varkappa$ tends to infinity.

$(\mathrm{d}\sigma/\mathrm{d}\Omega)_{cc}$ looks like a generalized Laute scattering cross-section arising from the chemical mixing of the liquid components, since it goes to

$$\tfrac{1}{2} \sum_{\alpha\beta} c_\alpha\, c_\beta\, (b_{\mathrm{Coh}\,\alpha} - b_{\mathrm{Coh}\,\beta})^2$$

as $\varkappa$ tends to infinity (each term $S\,c_\alpha\,c_\beta$ tending to $-c_\alpha\, c_\beta + c_\alpha\,\delta_{\alpha\beta}$).

Fournet, Faber and Ziman $^{1-3}$, prefer to define a third set of $\nu(\nu+1)/2$ independent partial interference functions $\mathcal{A}_{\alpha\beta}$** which tend to 1 when $\varkappa$ goes to infinity:

$$\mathcal{A}_{\alpha\beta}(\varkappa) = \mathcal{N}_{\alpha\beta}(\varkappa)/c_\alpha\, c_\beta + 1 - \delta_{\alpha\beta}/c_\alpha \tag{22}$$

(with $\mathcal{A}_{\alpha\beta} = \mathcal{A}_{\beta\alpha}$)
and write the coherent cross-section in the form

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_{\mathrm{Coh}} = \tfrac{1}{2} \sum_{\alpha\beta} c_\alpha\, c_\beta\, (b_{\mathrm{Coh}\,\alpha} - b_{\mathrm{Coh}\,\beta})^2 + \sum_{\alpha\beta} c_\alpha\, c_\beta\, b_{\mathrm{Coh}\,\alpha}\, b_{\mathrm{Coh}\,\beta}\, \mathcal{A}_{\alpha\beta}(\varkappa) \tag{23}$$

where the Laue scattering cross-section is explicitly seen. However, the physical meaning of these partial interference functions is not obvious since they are not related to any simple correlation function.

5. Equivalence between Laue and Incoherent Scattering Cross-sections

From the neutron scattering point of view a monatomic liquid may be considered as a liquid alloy made of several components having different Fermi scattering lengths. If a_p and I_p are respectively the isotopic abundance and nuclear spin of isotope p, $b_{\mathrm{p}+}$ and $b_{\mathrm{p}-}$ its Fermi scattering length when its spin is respectively parallel or antiparallel to the neutron spin, the concentrations of nuclei having scattering lengths $b_{\mathrm{p}+}$ and $b_{\mathrm{p}-}$ are, for an unpolarized nuclear target:

$$c_{\mathrm{p}+} = a_\mathrm{p}\,\frac{I_\mathrm{p}+1}{2\,I_\mathrm{p}+1}\,, \quad c_{\mathrm{p}-} = a_\mathrm{p}\,\frac{I_\mathrm{p}}{2\,I_\mathrm{p}+1}\,,$$

and the total cross-section may be written

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \tfrac{1}{2} \sum_{\mathrm{psp's'}} c_{\mathrm{ps}}\, c_{\mathrm{p's'}}\, (b_{\mathrm{ps}} - b_{\mathrm{p's'}})^2 + \sum_{\mathrm{psp's'}} c_{\mathrm{ps}}\, c_{\mathrm{p's'}}\, b_{\mathrm{ps}}\, b_{\mathrm{p's'}}\, \mathcal{A}_{\mathrm{psp's'}}(\varkappa)$$

where the index s stands for + or − and $\mathcal{A}_{\mathrm{psp's'}}$ are the "partial isotopic interference functions". Making use of the relations

$$\sum_{\mathrm{ps}} c_{\mathrm{ps}} = 1 \quad \sum_{\mathrm{ps}} c_{\mathrm{ps}}\, b_{\mathrm{ps}}^2 = \langle b^2 \rangle_I \quad \sum_{\mathrm{ps}} c_{\mathrm{ps}}\, b_{\mathrm{ps}} = \langle b \rangle_I = b_{\mathrm{Coh}}$$

one obtains immediately

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \langle b^2 \rangle_I - \langle b \rangle_I{}^2 + \sum_{\mathrm{psp's'}} c_{\mathrm{ps}}\, c_{\mathrm{p's'}}\, b_{\mathrm{ps}}\, b_{\mathrm{p's'}}\, \mathcal{A}_{\mathrm{psp's'}}(\varkappa) \tag{24}$$

where the Laue cross-section has now been expressed as the well known incoherent scattering cross-section. If the isotopes and nuclear spins are randomly distributed, the functions $\mathcal{A}_{\mathrm{psp's'}}(\varkappa)$ do not depend on the indices p, s, p′, s′ and formula (24) reduces, as usual, to

$$\mathrm{d}\sigma/\mathrm{d}\Omega = \langle b^2 \rangle_I - \langle b \rangle_I{}^2 + \langle b \rangle_I{}^2\, \mathcal{A}(\varkappa)\,.$$

On the contrary, in the case of polarized neutron scattering by liquid He_3 one must introduce partial spin interference functions $\mathcal{A}_{\uparrow\uparrow}$ and $\mathcal{A}_{\downarrow\uparrow}$ in order to describe the differences in correlation between parallel and antiparallel nuclear spin pairs.

6. Integral Relations

From the definition (19) of the partial number structure factors including the function $\Phi(\varkappa)$, and using the equation

$$\frac{1}{(2\,\pi)^3} \int e^{i\varkappa \boldsymbol{r}}\, \mathrm{d}_3\varkappa = \delta(\boldsymbol{r})$$

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* From expressions (15), (16) and (19) similar expressions volve any $\Phi(\varkappa)$ function.

** From formulae (13), (14), (15), (16) and (22) it is easy to show that:

$$c_\alpha\, c_\beta\, \mathcal{A}_{\alpha\beta} = c_\alpha\, c_\beta\, S_{NN} + c_\alpha\, S_{Nc_\beta} + c_\beta\, S_{Nc_\alpha} + S_{c_\alpha c_\beta} + c_\alpha\, c_\beta - c_\alpha\, \delta_{\alpha\beta}\,,$$

$$S_{NN} = \sum_{\alpha\beta} c_\alpha\, c_\beta\, \mathcal{A}_{\alpha\beta}\,,$$

$$S_{Nc_\alpha} = c_\alpha [\sum_\gamma c_\gamma\, \mathcal{A}_{\alpha\gamma} - \sum_{\gamma\delta} c_\gamma\, c_\delta\, \mathcal{A}_{\gamma\delta}]\,,$$

$$S_{c_\alpha c_\beta} = -c_\alpha\, c_\beta [\sum_\gamma c_\gamma (\mathcal{A}_{\alpha\gamma} + \mathcal{A}_{\beta\gamma}) - \sum_{\gamma\delta} c_\gamma\, c_\delta\, \mathcal{A}_{\gamma\delta} - \mathcal{A}_{\alpha\beta} + 1] + c_\alpha\, \delta_{\alpha\beta}\,.$$

it is easy to show the integral relation

$$\frac{1}{(2\pi)^3}\int[\mathcal{N}_{\alpha\beta}(\varkappa)-c_\alpha\,\delta_{\alpha\beta}]\,\mathrm{d}_3\varkappa=-\frac{N}{V}\,c_\alpha\,c_\beta\,.$$

In the same way, one also obtains

$$\frac{1}{(2\pi)^3}\int[S_{NN}(\varkappa)-1]\,\mathrm{d}_3\varkappa=-\frac{N}{V}\,,$$

$$\int S_{Nc_\alpha}(\varkappa)\,\mathrm{d}_3\varkappa=0\,,$$

and

$$\int[S_{c_\alpha c_\beta}(\varkappa)+c_\alpha\,c_\beta-c_\alpha\,\delta_{\alpha\beta}]\,\mathrm{d}_3\varkappa=0\,.$$

The integral relations relative to partial interference functions $\mathcal{A}_{\alpha\beta}(\varkappa)$ have already been given by Enderby, North and Egelstaff[6].

7. Inequality Relations

If we consider the partial liquid composed of elements α and β, the corresponding coherent cross-section must be a positive quadratic form in $b_{\mathrm{Coh}\,\alpha}$ and $b_{\mathrm{Coh}\,\beta}$. Whe thus obtain the necessary and sufficient inequality relations

$$\mathcal{N}_{\alpha\alpha}(\varkappa)\geqq 0\,, \tag{25}$$

$$\mathcal{N}^2_{\alpha\neq\beta}(\varkappa)\leqq\mathcal{N}_{\alpha\alpha}(\varkappa)\,\mathcal{N}_{\beta\beta}(\varkappa)\,. \tag{26}$$

The interpretation of inequality (25) is simple since it arises from the fact that

$$\mathcal{N}_{\alpha\alpha}(\varkappa\neq 0)=\frac{1}{N}\,\langle|\sum_i\exp\{i\,\varkappa\,\mathbf{R}_i{}^\alpha\}|^2\rangle$$

is proportional to the cross-section of partial liquid α. Relations (25) and (26) are equivalent to those derived by Enderby, North and Egelstaff[6] in binary alloys:

$$c_\alpha\,\mathcal{A}_{\alpha\alpha}+1-c_\alpha\geqq 0$$

and

$$c_\alpha\,c_\beta\,(\mathcal{A}_{\alpha\neq\beta}-1)^2\leqq(c_\alpha\,\mathcal{A}_{\alpha\alpha}+1-c_\alpha)\,(c_\beta\,\mathcal{A}_{\beta\beta}+1-c_\beta)\,.$$

It is worthwhile to notice that $\mathcal{A}_{\alpha\alpha}(\varkappa)$ partial structure factors which are not proportional to any cross-section, need not be positive.

A striking example is given by a dilute binary alloy ($c_2\ll 1$) in which

$$\mathcal{A}_{11}(\varkappa)\gtrsim 0$$

(a natural result, since the liquid then looks like a pure 1 liquid) whereas

$$\mathcal{A}_{22}(\varkappa)\gtrsim -1/c_2$$

is almost unrestricted in sign.

Integral as well as inequality relations are useful in practice when checking the partial structure factors since they involve the shape of these functions over the whole $\varkappa$ range.

8. Limiting $\varkappa=0$ Values

Limiting values of the partial structure factors when $\varkappa$ tends to 0 may be calculated from the thermodynamical properties of the system and are used when normalizing count rates obtained by experiment to the cross-sections.

From the definition of the partial structure factors $\mathcal{N}_{\alpha\beta}(\varkappa)$ these limiting values are proportional to the correlated fluctuations in the partial numbers

$$\mathcal{N}_{\alpha\beta}(0)=\frac{\langle(N_\alpha-\overline{N}_\alpha)\,(N_\beta-\overline{N}_\beta)\rangle}{\overline{N}} \tag{27}$$

$$=\frac{\langle\Delta N_\alpha\,\Delta N_\beta\rangle}{\overline{N}}=\frac{\xi_{\alpha\beta}}{\overline{N}}\,.$$

According to Hill[7], these fluctuations may be expressed with the aid of the second order derivatives of the Gibbs free energy:

$$\xi_{\alpha\beta}=k_B\,T\,\frac{\partial\Delta/\partial g_{\alpha\beta}}{\Delta}$$

where k_{B} is the Boltzmann constant, T the temperature and Δ the determinant with elements

$$g_{\alpha\beta}=\left(\frac{\partial\mu_\alpha}{\partial N_\beta}\right)_{T,P,N'_\beta}+\frac{v_\alpha\,v_\beta}{V\chi}$$

$$=\left(\frac{\partial^2 G}{\partial c_\alpha\,\partial c_\beta}\right)_{T,P,C'_{\alpha\beta}}\frac{(1-c_\alpha)\,(1-c_\beta)}{N^2}+\frac{v_\alpha\,v_\beta}{V\chi}$$

In this expression μ_α is the chemical potential of element α, $v_\alpha=(\partial\mu_\alpha/\partial p)_{T,N}$ its partial volume, G the Gibbs free energy of the alloy and

$$\chi=-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{\mathrm{T,N}}$$

its compressibility. A partial derivative indexed with, for example, $N_\beta{}'$ means that all partial numbers except N_β are kept constant.

In the special case of binary alloys, Eq. (27) gives

$$\mathcal{N}_{11}(0)=\left(\frac{c_1{}^2\,V\chi}{N}+\frac{v_2{}^2\,N}{G''}\right)k_B\,T\,\frac{N^2}{V^2}{}^*\,,$$

$$\mathcal{N}_{12}(0)=\left(\frac{c_1\,c_2\,V\chi}{N}-\frac{v_1\,v_2\,N}{G''}\right)k_B\,T\,\frac{N^2}{V^2}$$

where

$$G''=\partial^2 G/\partial c_1{}^2\,.$$

* $\mathcal{N}_{22}(0)$ is obtained by a trivial cyclic permutation.

In the same way, it is easy to show from relations (14), (15) and (16) that

$$S_{NN}(0)=\frac{\langle \varDelta N^2\rangle}{\overline{N}}=\frac{1}{\overline{N}}\sum_{\alpha\beta}\xi_{\alpha\beta}\,, \tag{28}$$

$$S_{Nc_\alpha}(0)=\langle \varDelta N\,\varDelta c_\alpha\rangle=\frac{1}{\overline{N}}\,\Big(\sum_{\gamma}\xi_{\alpha\gamma}-\overline{c}_\alpha\sum_{\gamma\delta}\xi_{\gamma\delta}\Big)\,, \tag{29}$$

$$S_{c_\alpha c_\beta}(0)=\overline{N}\,\langle \varDelta\, c_\alpha\,\varDelta c_\beta\rangle$$

$$=\frac{1}{\overline{N}}\,\Big(\xi_{\alpha\beta}-\overline{c}_\alpha\sum_{\gamma}\xi_{\beta\gamma}-\overline{c}_\beta\sum_{\gamma}\xi_{\alpha\gamma}+\overline{c}_\alpha\,\overline{c}_\beta\sum_{\gamma\delta}\xi_{\gamma\delta}\Big)\,. \tag{30}$$

9. Size Effects

It was already emphasized that the cross-section expressions (18) and (20) are valid except near $\varkappa=0$ since the terms involving $\Phi(\varkappa)$ must then be dropped in the structure factor definitions. The exact expression of the coherent cross-section is

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_{\mathrm{Coh}}=\sum_{\alpha\beta}b_{\mathrm{Coh}\,\alpha}\,b_{\mathrm{Coh}\,\beta}\,\mathcal{N}'_{\alpha\beta}(\varkappa) \tag{31}$$

with

$$\mathcal{N}'_{\alpha\beta}(\varkappa)=\mathcal{N}_{\alpha\beta}(\varkappa)+\frac{N_\alpha N_\beta}{\overline{N}}\,|\,\Phi(\varkappa)\,|^{2}\,. \tag{32}$$

These modified partial number structure factors have a central peak at $\varkappa=0$ whose height is equal to $\overline{N_\alpha N_\beta}/\overline{N}$ and whose width $\varDelta\varkappa$ is inversely proportional to the cubic root L of the scattering volume V [8]. One thus obtains

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_{\mathrm{Coh}}(0)=\sum_{\alpha\beta}b_{\mathrm{Coh}\,\alpha}\,b_{\mathrm{Coh}\,\beta}\,\mathcal{N}'_{\alpha\beta}(0) \tag{33}$$

$$=\frac{1}{\overline{N}}\sum_{\alpha\beta}b_{\mathrm{Coh}\,\alpha}\,b_{\mathrm{Coh}\,\beta}\,\overline{N_\alpha\,N_\beta}$$

and

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_{\mathrm{Coh}}\left(\frac{1}{\mathrm{d}}\gg\varkappa\gg\frac{1}{L}\right)=\sum_{\alpha\beta}b_{\mathrm{Coh}\,\alpha}\,b_{\mathrm{Coh}\,\beta}\,\mathcal{N}_{\alpha\beta}(0)$$

$$=\frac{1}{\overline{N}}\sum_{\alpha\beta}b_{\mathrm{Coh}\,\alpha}\,b_{\mathrm{Coh}\,\beta}\,(\overline{N_\alpha\,N_\beta}-\overline{N}_\alpha\,\overline{N}_\beta) \tag{34}$$

where d is of the order of the atomic diameter.

In most cases, the sample size is so large that $\varDelta\varkappa$ is very small and the central peak cannot be distinguished from the direct beam. The cross-section measured at small scattering angles is then given by (34). However, for very small scattering volumes, the central peak is wide enough to be measured and formula (31) holds.

In the same way, if one uses the generalized Bhatia-Thornton formalism, expression (20) becomes

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_{\mathrm{Coh}}=b^{2}_{\mathrm{Coh}}S'_{NN}(\varkappa)+2\,b_{\mathrm{Coh}}\sum_{\alpha}b_{\mathrm{Coh}\,\alpha}\,S'_{Nc_\alpha}$$

$$-\tfrac{1}{2}\sum_{\alpha\beta}(b_{\mathrm{Coh}\,\alpha}-b_{\mathrm{Coh}\,\beta})^{2}\,S'_{c_\alpha c_\beta}$$

where $S_{NN}(\varkappa)$ is replaced by

$$S'_{NN}(\varkappa)=S_{NN}(\varkappa)+\overline{N}\,|\,\Phi(\varkappa)|^{2} \tag{35}$$

with $S'_{NN}(0)=\overline{N^2}/\overline{N}$

instead of $S_{NN}(0)=(\overline{N^2}-\overline{N}^2)/\overline{N}\,.$

However, $S_{Nc\alpha}$ and $S\,c_\alpha\,c_\beta$ remain unchanged since they do not involve any $\Phi(\varkappa)$ function:

$$S'_{Nc_\alpha}=S_{Nc_\alpha},\quad S'_{c_\alpha c_\beta}=S_{c_\alpha c_\beta}\,.$$

Thus small angle scattering due to size effect only affects $S'_{NN}(\varkappa)$ whereas the values of $S'_{Nc\alpha}$ and $S'_{c_\alpha c_\beta}$ at $\varkappa=0$ are always given by formulae (29) and (30).

10. Isotropic Approximation

In this section we deal with $\varkappa$ values larger than $\varDelta\varkappa$ and drop, as usual, the $\Phi(\varkappa)$ functions involved in the structure factor expressions.

In the case of liquids, the thermal average which is involved in cross-section expressions ensures that all the orientations of pair vectors $\boldsymbol{R}_{ij}^{\alpha\beta}=\boldsymbol{R}_j^{\beta}-\boldsymbol{R}_i^{\alpha}$ having the same modulus are equally probable, whatever the size of the sample. In this condition the cross-section does not depend on the orientation of $\boldsymbol{\varkappa}$. In the case of amorphous materials, where each scattering centre has a well defined mean position, this averaging process does not hold. For large enough samples, where the huge number of vectors $\boldsymbol{R}_{ij}^{\alpha\beta}$ having the same modulus $R_{ij}^{\alpha\beta}$ ensures that all their orientations are equally probable, the cross-section is still isotropic. This is no longer true for a small amorphous grain where large distances $R_{ij}^{\alpha\beta}$ are represented by a small number of pairs and the cross-section does depend on the orientation of $\boldsymbol{\varkappa}$ [9]. However, in this section we deal only with the isotropic case where according to Debye, Zernike and Prins [10, 11], each term $\exp\{i\,\boldsymbol{\varkappa}(\boldsymbol{R}_j^{\beta}-\boldsymbol{R}_i^{\alpha})\}$ with $i,\alpha\neq j,\beta$ may be replaced by its mean value over the solid angles

$$\sin(\varkappa\,R_{ij}^{\alpha\beta})/\varkappa\,R_{ij}^{\alpha\beta}$$

Thus

$$\mathcal{N}_{\alpha\alpha}(\varkappa) = c_\alpha + \frac{1}{N} \sum_{i \neq j} \frac{\sin(\varkappa R_{ij}^{\alpha\alpha})}{\varkappa R_{ij}^{\alpha\alpha}} = c_\alpha + \frac{2}{N} \sum_{i > j} \frac{\sin(\varkappa R_{ij}^{\alpha\alpha})}{\varkappa R_{ij}^{\alpha\alpha}}$$

(in the first expression of $\mathcal{N}_{\alpha\alpha}$ each $i\alpha - j\alpha$ pair is counted twice whereas it is only counted once in the second expression)

$$\mathcal{N}_{\alpha \neq \beta}(\varkappa) = \frac{1}{N} \sum_{ij} \frac{\sin(\varkappa R_{ij}^{\alpha\beta})}{\varkappa R_{ij}^{\alpha\beta}}$$

(in this expression each pair $i\alpha - j\beta$ is counted once since $R_{ij}^{\alpha\beta}$ has an α origin)

$$S_{NN}(\varkappa) = 1 + \frac{1}{N} \sum_{i\alpha \neq j\beta} \frac{\sin(\varkappa R_{ij}^{\alpha\beta})}{\varkappa R_{ij}^{\alpha\beta}} ,$$

or

$$\mathcal{A}_{\alpha\alpha}(\varkappa) = 1 + \frac{1}{N c_\alpha^2} \sum_{i \neq j} \frac{\sin(\varkappa R_{ij}^{\alpha\alpha})}{\varkappa R_{ij}^{\alpha\alpha}} ,$$

$$\mathcal{A}_{\alpha \neq \beta}(\varkappa) = 1 + \frac{1}{N c_\alpha c_\beta} \sum_{ij} \frac{\sin(\varkappa R_{ij}^{\alpha\beta})}{\varkappa R_{ij}^{\alpha\beta}} .$$

These sum formulae are mainly used by computer model designers who deduce partial structure factors from pair distance calculations. On the other hand, Fournet, Faber and Ziman [1-3] give an integral representation for the partial interference functions

$$\mathcal{A}_{\alpha\beta}(\varkappa) = 1 + \frac{N}{V} \int \frac{\sin(\varkappa r)}{\varkappa r} [P_{\alpha\beta}(r) - 1] \, 4 \pi r^2 \, \mathrm{d}r$$

where $P_{\alpha\beta}(r)$ is the probability per unit volume of finding an α atom at a distance r from another β atoms normalized in such a way that $P_{\alpha\beta}(r)$ goes to unity for large r. This integral representation is more used by experimentalists who deduce pair correlation functions from measured $\mathrm{d}\sigma/\mathrm{d}\Omega$ curves by the inverse formula

$$P_{\alpha\beta}(r) = 1 + \frac{V}{N} \frac{1}{(2\pi)^3} \int \frac{\sin(\varkappa r)}{\varkappa r} \cdot [\mathcal{A}_{\alpha\beta}(\varkappa) - 1] \, 4 \pi \varkappa^2 \, \mathrm{d}\varkappa .$$

Conclusion

In order to describe the structure of multicomponent liquid or amorphous alloys, we have introduced in this paper a set of structure factors which are associated to the different correlations between the numbers of particles of all chemical species. Owing to the simplicity of the physical meaning of these structure factors, the corresponding inequality relations and limiting values are easy to express. This formalism is thus particularly well adapted to the study of alloys of more than two components, for which the interpretation of Fournet-Faber-Ziman and generalized Bhatia-Thornton theories is more complex.

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