

Number of independent partial structure factors for a disordered n -component system

David L. Price

Argonne National Laboratory, Argonne, Illinois 60439

Alfredo Pasquarello

Institut Romand de Recherche Numérique en Physique des Matériaux, IN-Ecublens, CH-1015 Lausanne, Switzerland

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$n(n+1)/2$ independent diffraction measurements are needed to obtain complete partial structure information for a disordered n -component condensed system. A previous assertion that only n of these are independent is shown to be inapplicable, for different reasons, to both the three-dimensional partial structure factors $S_{ab}(\mathbf{Q})$ and the orientational averages $S_{ab}(Q)$. The fluctuations of $S_{ab}(\mathbf{Q})$ about $S_{ab}(Q)$ and the effects of thermal motion are discussed. [S0163-1829(99)00401-4]

A number of years ago Dolgopolsky and Johnson¹ challenged the accepted notion that $n(n+1)/2$ independent diffraction measurements were needed to obtain complete partial structure information for an n -component condensed system in the form of a gas, liquid or glass. This assertion was immediately challenged on various grounds,^{2,3} and a few years later was shown to be misleading if resolution effects were not considered.⁴ Nevertheless, the basic reason why the assertion of Ref. 1 is not applicable to disordered systems is not generally appreciated and, now that systematic measurements with coherent x-ray beams are possible,^{5,6} it appears worthwhile to revisit this issue.

In conventional notation, the argument of Ref. 1 can be stated as follows. The partial structure factor for the element pair (a,b) can be written⁷

$$S_{ab}(\mathbf{Q}) = \frac{1}{(N_a N_b)^{1/2}} \sum_{i \in a, j \in b} \exp[i\mathbf{Q} \cdot (\mathbf{r}_i - \mathbf{r}_j)] - (N_a N_b)^{1/2} \delta_{\mathbf{Q}\mathbf{0}}, \quad (1)$$

where \mathbf{r}_i is the position of the i th particle at the time of the measurement. By rearranging terms, it is clear that

$$S_{aa}(\mathbf{Q})S_{bb}(\mathbf{Q}) = S_{ab}(\mathbf{Q})S_{ab}^*(\mathbf{Q}). \quad (2)$$

If the system has inversion symmetry,

$$S_{ab}(-\mathbf{Q}) = S_{ab}(\mathbf{Q}), \quad (3)$$

and since

$$S_{ab}^*(\mathbf{Q}) \equiv S_{ab}(-\mathbf{Q}),$$

it follows that

$$S_{ab}(\mathbf{Q}) = [S_{aa}(\mathbf{Q})S_{bb}(\mathbf{Q})]^{1/2}, \quad (4)$$

thus there are only n -independent partial structure factors, which can be completely determined by n diffraction experiments.

This result was challenged by Ruppertsberg and Schirmacher² on the basis that $S_{ab}(\mathbf{Q})$ is in general complex for a disordered system and Eqs. (3),(4) do not hold. Ballentine³ accepted the validity of Eq. (2) in the case of

atoms in fixed positions but asserted that for systems undergoing thermal motion the sum in Eq. (1) must be replaced by its time average over the duration of the measurement or, equivalently for a system in thermal equilibrium, by its ensemble average, in which case Eq. (2) no longer holds. In the context of the speckle in the diffraction patterns of disordered materials, Ludwig⁴ pointed out that Eq. (2) is mathematically valid but produces misleading effects if resolution effects are not taken into account. In this report we examine the applicability of Eq. (2), and the objections that have been raised to it, in the case of a simple network glass.

Figure 1 shows the results for $S_{ab}(\mathbf{Q})$ for a model generated by an *ab initio* molecular-dynamics simulation that gives a good representation of both the structure⁸ and dynamics⁹ of vitreous SiO₂. The three types of symbol denote $S_{ab}(\mathbf{Q})$ for \mathbf{Q} along the three cube axes of the simulation cell. [Only one direction need be shown along a given axis because $S_{ab}(-\mathbf{Q}) = S_{ab}(\mathbf{Q})^*$]. It can be verified that Eq. (2) holds exactly for each value of \mathbf{Q} ; Eqs. (3),(4) do not of course hold since at this level there is no inversion symmetry and $S_{ab}(\mathbf{Q})$ is complex for $a \neq b$. As is now well known, $S_{ab}(\mathbf{Q})$ in this form represents the speckle pattern⁴⁻⁶ which can be observed in the situation where the coherence volume in the diffraction measurement is larger than the irradiated volume of the sample.¹⁰ In conventional diffraction measurements this is not, of course, the case, and one measures an average of $S_{ab}(\mathbf{Q})$ over many coherence volumes which averages out the fluctuations seen in Fig. 1. The measured quantity, $S_{ab}(Q)$, is most simply derived from a simulation model by calculating the orientational average

$$S_{ab}(Q) = \frac{1}{4\pi} \int S_{ab}(\mathbf{Q}) d\Omega.$$

For a model of the type discussed here, which satisfies periodic boundary conditions, the average is carried out over the star of values

$$\mathbf{Q} = \frac{2\pi}{L} (h, k, l) \quad \text{with } |\mathbf{Q}| = Q,$$

where L is the side of the cubic simulation cell and h, k, l are integers. This is found to give a reasonable representation of

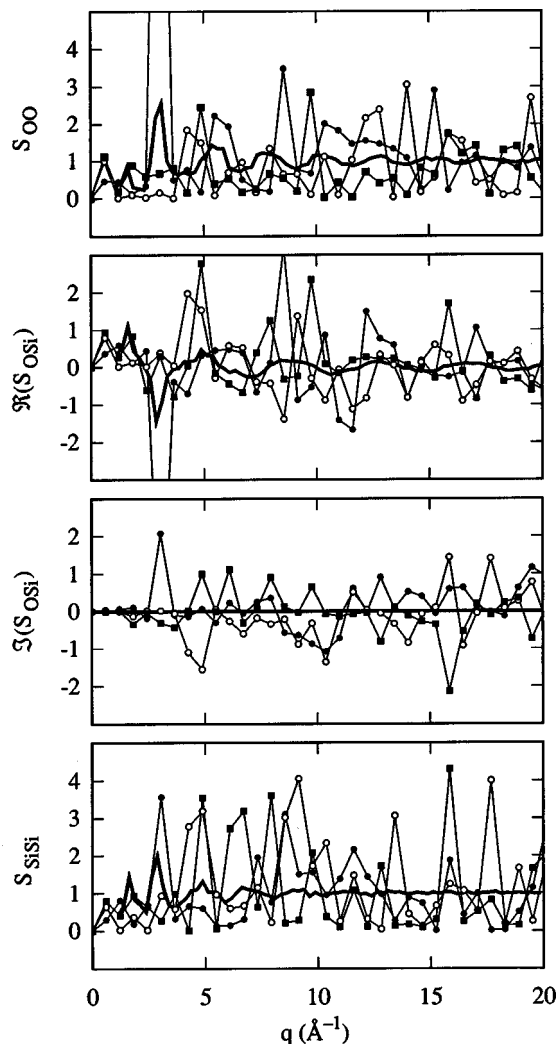


FIG. 1. Partial structure factors for a structural model of vitreous SiO_2 generated by an *ab initio* molecular-dynamics simulation (Ref. 8). Symbols: $S_{ab}(\mathbf{Q})$ for \mathbf{Q} along [100] (closed circles), [010] (open circles), and [001] (squares) directions of the cubic simulation cell; the thin lines joining the symbols are a guide to the eye. Heavy lines: orientationally averaged $S_{ab}(Q)$.

the experimentally measured structure factors.⁸ $S_{ab}(Q)$ derived in this way is a smoothly varying, necessarily real, function of Q . Its values are shown by the heavy lines in Fig. 1 and are seen to average out the large fluctuations in $S_{ab}(\mathbf{Q})$ as expected.

For large values of \mathbf{Q} , the magnitude of the fluctuations can be estimated by treating $x_{ij} = \mathbf{Q} \cdot (\mathbf{r}_i - \mathbf{r}_j)$ as a random variable except for $i=j$ when $x_{ii}=0$. Defining a standard deviation in the fluctuations

$$\sigma[S_{ab}] = \langle S_{ab}(\mathbf{Q}) - S_{ab}(Q) \rangle_{\text{rms}},$$

where rms signifies a root-mean square average over a set of large values of \mathbf{Q} , one obtains the result¹¹⁻¹³

$$\sigma[S_{aa}] = 1, \quad (5)$$

$$\sigma[\text{Re}(S_{ab})] = \sigma[\text{Im}(S_{ab})] = \frac{1}{\sqrt{2}}, \quad a \neq b.$$

Calculation for the simulation discussed here, averaging over values of \mathbf{Q} from (0,0,20) to (0,0,100) \AA^{-1} , gives

$$\sigma[S_{00}] = 0.95, \quad \sigma[S_{\text{SiSi}}] = 0.98, \quad (6)$$

$$\sigma[\text{Re}(S_{\text{Osi}})] = 0.64, \quad \sigma[\text{Im}(S_{\text{Osi}})] = 0.61,$$

reasonably close to the ideal values in spite of the small size of the model. Calculations for a larger model give values closer to the ideal ones.

The product of two orientational averages is not the same as the average of the product, and Eq. (2) does not hold for $S_{ab}(Q)$ even for a static system (i.e., a classical solid at low temperature), or for a polycrystalline sample even when the underlying crystal structure has a center of inversion. This is easily seen by considering a specific term in Eq. (2): setting $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$,

$$j_0(Qr_{ij})j_0(Qr_{kl}) \neq j_0(Qr_{il})j_0(Qr_{kj})$$

in general, even though $\mathbf{r}_{ij} + \mathbf{r}_{kl} = \mathbf{r}_{il} + \mathbf{r}_{kj}$. Thus, Eq. (4) does not hold for either $S_{ab}(\mathbf{Q})$ or $S_{ab}(Q)$, and there are therefore $n(n+1)/2$ independent partial structure factors in both cases, as generally accepted.

Equation (4) is, of course, applicable in the case of a single crystal with inversion symmetry, even for a conventional diffraction measurement, since then the structure of the sample itself supplies the necessary coherence. When thermal motion is taken into account, Eq. (4) still applies to the elastic scattering in the case of isotropic, harmonic Debye-Waller factors.¹⁴

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