



# Can a periodic boundary model reproduce the longer-range density fluctuations in a real amorphous material?☆



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## ABSTRACT

Whereas the conventional definition of the static structure factor,  $S(Q)$ , means that, for any sample or structural model, its value at zero  $Q$ ,  $S(0)$ , is identically equal to zero, the structures of ideally-disordered materials, such as single-phase liquids and amorphous solids, incorporate long-range density fluctuations that are characterised by a non-zero limiting value ( $S_0$ ) of  $S(Q \neq 0)$  as  $Q \rightarrow 0$ . An analysis of these density fluctuations in terms of their Fourier components leads to the definition of an ideally-disordered material as one that exhibits a continuous, isotropic distribution of Fourier wavelengths,  $A(\Lambda)$ , that decays asymptotically to zero at  $\Lambda = \infty$ . On the other hand, a similar analysis for a periodic boundary model reveals that the form of the intermediate-range order at higher inter-atomic distances,  $r$ , and that of the long-range density fluctuations are fundamentally different from those of a real amorphous material. The severely limited number of (especially the longer) allowed Fourier wavelengths,  $\Lambda$ , coupled with their strictly defined orientations within the unit cell of a periodic boundary model, means that such a model is inherently crystalline, and that no amount of orientational (polycrystalline) averaging can overcome this problem. The various methods of deriving  $S(Q)$  for both periodic-boundary and cluster models are discussed, and it is shown that, since a periodic boundary model is not ideally-disordered, a polycrystalline average does not yield a consistent value for  $S_0$ , but one that is dependent on its exact method of calculation. It is therefore concluded that, to investigate the longer-range density fluctuations in amorphous materials, it is essential to employ a cluster model, rather than one generated with a periodic boundary.

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## 1. Introduction

To date, the vast majority of computer modeling/simulation studies of amorphous materials have employed periodic boundary conditions, and have concentrated on the short- and earlier intermediate-range (i.e. local) structure and the properties derived therefrom. More recently, however, the possibility of generating large atomistic models, such as those of amorphous silicon [1,2] and vitreous silica [1], together with renewed interest in the form of the longer-range density fluctuations in amorphous materials, has led to attempts to use such models to calculate the limit, as the scattering vector magnitude,  $Q$ , approaches zero, of the static structure factor,  $S(Q)$ . For both of these single-component materials, composition fluctuations are absent, and so  $S(Q)$ , is solely the result of spatial fluctuations in atomic number density. The question thus arises as to the form of these longer-range density fluctuations in different types of amorphous material, as compared to those in the structural models. For the former, they depend on the

detailed preparation conditions and subsequent thermal history, and for the latter they reflect the method of generating the model co-ordinates. ***There is, of course, absolutely no reason why the form of these density fluctuations should be the same for different types of amorphous material, or model.*** This is particularly true of atomistic structural models generated with a periodic boundary, for which it will be demonstrated that the density fluctuations are inherently anisotropic (crystalline), and do not match those in a real amorphous solid.

Whilst the role of long-wavelength real-space density fluctuations in determining the magnitude of  $S(Q)$  at low scattering vector magnitudes,  $Q$ , is well established, it is not generally appreciated that the short- and intermediate-range order are similarly related to the shorter-wavelength fluctuations in the atomic number density. In addition, there is considerable confusion in the literature as to the effect of periodic boundary conditions on the extraction of both the static structure factor,  $S(Q)$ , and the real-space total correlation function,  $t(r)$ , for a structural model with a periodic boundary. Hence the various methods of calculating these functions will be discussed, and recommendations made as to the optimum method in each case, whilst taking into account the *raison d'être* for the model in question.

For simplicity, the theoretical background in this paper is restricted to elemental materials, but identical arguments apply to chemically-

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ordered binary systems, such as vitreous silica, and to the composition fluctuations in materials that are not chemically ordered. Similarly, the discussion of periodic-boundary models will be limited to those having a pseudo-cubic unit cell, such as the “Sillium” model of amorphous Si/Ge due to Wooten & Weaire [3–5] used here. This model only has 216 atoms in the unit cell, which limits both the statistical accuracy and the reciprocal-space resolution of  $S(Q)$ , but these are certainly adequate to illustrate the general principles discussed in this paper.

## 2. Small- $Q$ scattering

For an isotropic, single-phase, single-component amorphous material, such as amorphous silicon or vitreous silica, the limiting behaviour, as  $Q \rightarrow 0$ , of the static structure factor,  $S(Q)$ , as determined from small-angle neutron scattering (SANS) or small-angle X-ray scattering (SAXS) experiments takes the form

$$S(Q) = S_0 + c_2 Q^2, \quad (1)$$

in which  $S_0$  is the zero- $Q$  limit and  $c_2$  is a constant, as may be seen from Fig. 1 [6], which shows such a fit to SANS data for vitreous silica. Note that  $S(Q)$  is an even function, and so there is no term in  $Q$ ; i.e.  $c_1 = 0$ . Strictly, of course, small- $Q$  scattering measurements can only be recorded down to a minimum scattering vector magnitude,  $Q_{\min}$ , but there is no experimental evidence that  $S(Q)$  for such a macroscopic sample is not continuous down to exceedingly small values of  $Q$  (see Section 5).

In the case of a liquid [7], the value of  $S_0$  at temperature,  $T$ , is given by

$$S_0 = \rho^0 k_B T \chi(T), \quad (2)$$

where  $\rho^0$  is its average number density and

$$\chi(T) = \chi_0(T) + \chi_\infty(T) \quad (3)$$

is its isothermal compressibility, which may be separated into topological,  $\chi_0(T)$ , and rigid network,  $\chi_\infty(T)$ , components [6,8]. The topological component, which arises from changes in the network topology resulting from a rearrangement of bonding, is only present for the liquid state, and disappears on passing into the (crystalline or amorphous) solid state, as may be seen from Fig. 2 of Ref. 6. The rigid network contribution does not involve changes in the network topology and, in the liquid state, can be measured at frequencies much higher than those associated with bond switching. Conversely, a measurement of the total  $\chi(T)$  for a liquid must be made using a low frequency or static technique [8].

A glass is formed by quenching the melt and, if it is assumed that the topological density fluctuations present in the super-cooled liquid at the glass transition temperature,  $T_g$ , (strictly the fictive temperature,  $T_f$ , which varies with the fluctuations in the average number density,  $\rho^0$ ) are “frozen-in” as the liquid is quenched through the glass transition region, then  $S_0$  for the glass may be calculated from this part of the

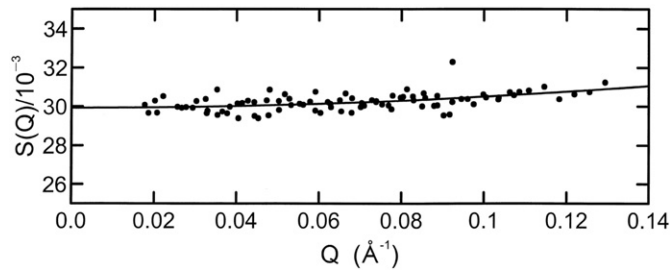


Fig. 1. SANS data for vitreous silica [6] (closed circles), together with a fit (solid line) to Eq. (1), with  $S_0 = 0.0299 \pm 0.0001$  and  $c_2 = 0.058 \pm 0.011$ . (Allowing for the uncertainty on the absolute normalisation increases the overall uncertainty on  $S_0$  to  $\pm 0.0020$ .)

isothermal compressibility of the super-cooled liquid at  $T_g$ , whilst correcting the rigid network component to the ambient temperature,  $T$  [6,8]:

$$\begin{aligned} S_0 &= \rho^0 k_B [T_g \{ \chi(T_g) - \chi_\infty(T_g) \} + T \chi_\infty(T)] \\ &= \rho^0 k_B [T_g \chi_0(T_g) + T \chi_\infty(T)]. \end{aligned} \quad (4)$$

For vitreous silica, the value of  $S_0$  from Eq. (4) (0.030 [6,8]) is in excellent agreement with the SANS data from Ref. 6 ( $S_0 = 0.0299 \pm 0.0020$ ) (see Table 1 of Ref. 6).

As indicated in Section 1, the longer-range density fluctuations in amorphous materials formed other than by melt-quenching, depend on the details of their preparation, and those for structural models on the method used in their generation. In particular, it should be noted that  $S_0$  for a **static** structural model only involves the contribution from  $\chi_0(T_g)$ , such that

$$S_0 = \rho^0 k_B T_g \chi_0(T_g). \quad (5)$$

Thus it is to be expected that the value obtained for  $S_0$  from a static model should be lower than that for the corresponding amorphous solid, as calculated from Eq. (4).

## 3. Static structure factor

The static structure factor,  $S(Q)$ , for an isotropic amorphous material is conventionally defined as

$$S(Q) = 1 + \int_0^\infty 4\pi r^2 [\rho(r) - \rho^0] \sin(Qr) / (Qr) dr. \quad (6)$$

The radial density function,  $\rho(r)$ , is, on average, the atomic number density at a distance  $r$  from an arbitrary origin atom, and  $\rho^0$  is the average number density for the sample as a whole. The first term (unity) on the right hand side of Eq. (6) is known as the self-scattering and the second as the distinct-scattering. Alternatively,

$$Q[S(Q) - 1] = \int_0^\infty d(r) \sin(Qr) dr, \quad (7)$$

in which  $Q[S(Q) - 1]$  is known as the interference function, and  $d(r)$  is the real-space differential correlation function,

$$d(r) = 4\pi r [\rho(r) - \rho^0] = t(r) - t^0(r). \quad (8)$$

$t(r)$  is the total correlation function,

$$t(r) = 4\pi r \rho(r), \quad (9)$$

and  $t^0(r)$  is the contribution from the average number density  $\rho^0$ ,

$$t^0(r) = 4\pi r \rho^0. \quad (10)$$

It is extremely important to note that the contribution from  $\rho^0$ ,  $S^0(Q)$ , is **specifically excluded** from the definition of  $S(Q)$ . For an infinite sample, the former gives rise to a  $\delta$ -function at  $Q = 0$  and, in the case of a (poly)-crystalline material is equivalent to the 000 Bragg reflection.

## 4. Structure factor at zero $Q$ , $S(0)$

For a finite sample/model of volume  $V_s$ , containing  $N_s$  atoms,

$$S(Q) = 1 + \int_0^\infty 4\pi r^2 [\rho(r) - \rho^0] F(r) \sin(Qr) / (Qr) dr, \quad (11)$$

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