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Connection between structural characteristics of glasses and their crystalline counterparts

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Abstract

It is demonstrated that the origin of the low- Q features in the static structure factor of disordered solids, such as the first sharp diffraction peak, can be understood by studying structural characteristics of their crystalline counterparts. The positionally disordered lattice models exhibit the first sharp diffraction peak at approximately the same position as in corresponding disordered structures. The availability of the exact solution for lattice models gives an opportunity to identify the reciprocal space vectors which contribute most to this peak.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Structural properties of disordered solids are of great importance in the field of disordered systems [1]. In spite of a big effort put into this area both from theoretical and experimental sides there are still unsolved problems of considerable interest. One of the main structural characteristics of solids which is available from x-ray and neutron diffraction experiments is the static structure factor, $S(Q)$, with Q being the magnitude of the scattering wavevector. The Fourier transform of the static structure factor gives information about the pair distribution function describing atomic density fluctuations on the microscopic level. Many disordered solids exhibit a sharp feature in the range of $Q \sim 1\text{--}2 \text{ \AA}^{-1}$ called the first sharp diffraction peak (FSDP) [2] the nature of which is still rather debatable [3–9].

Several models have been suggested for the origin of the FSDP over the years. Probably, the most popular explanation of the FSDP is provided by the presence of local quasi-crystalline planes (layers) or equivalently quasi-Bragg planes [2, 7, 8, 10, 11]. An alternative model relates the FSDP to the spatial arrangements of voids in glasses [12].

The aim of this paper is to present a simple model of the FSDP in topologically disordered solids which reveals its origin and is based on the use of pseudo-crystalline planes characteristic of relevant crystalline counterparts. Below, we calculate analytically the static structure factor for positionally disordered lattice models and then demonstrate that it can mimic at least

the FSDP in glasses. Availability of analytical expression for $S(Q)$ gives an opportunity to understand all the contributions to the FSDP in lattice models and hopefully in corresponding glasses.

2. Pair distribution function for disordered lattices

We start with the derivation of the analytical expression for the static structure factor in positionally disordered lattices. Let us consider a 3D regular lattice defined by unit cell vectors \mathbf{a}_i ($i = 1, \dots, 3$) with N_{uc} atoms in the unit cell characterized by position vectors \mathbf{R}_j ($j = 1, \dots, N_{\text{uc}}$). The unperturbed position vector, $\mathbf{r}_{\mathbf{n},j}^{(0)}$, of an arbitrary atom in the unit cell of the regular lattice is $\mathbf{r}_{\mathbf{n},j}^{(0)} = \mathbf{R}_j + \mathbf{a}_{\mathbf{n}}$ where $\mathbf{a}_{\mathbf{n}} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$ ($\mathbf{n} = (n_1, n_2, n_3) \in \mathbb{Z}^3$). Therefore the set of vectors $\{\mathbf{r}_{\mathbf{n},j}^{(0)}\}$ defines a crystalline atomic lattice of any symmetry (e.g. a Bravais lattice for $j = 1$). Assume that a static stochastic independent displacement field, $\mathbf{u}_{\mathbf{n},j}$ is applied to such a lattice, so that the atomic position vectors are given by $\mathbf{r}_{\mathbf{n},j} = \mathbf{r}_{\mathbf{n},j}^{(0)} + \mathbf{u}_{\mathbf{n},j}$ with $\mathbf{u}_{\mathbf{n},j}$ being random vectors normally (for concreteness) distributed around zero expectation values, $E(\mathbf{u}_{\mathbf{n},j}) = 0$. The atoms within the unit cell can be of different types, such that we assume possible different variances for each species, but consider, for simplicity, only the isotropic displacement field, $\text{Var}(u^{(\alpha)})_{\mathbf{n},j} = \sigma_j^2$, where superscript $\alpha = 1, \dots, 3$ marks the Cartesian directions. The normal distributions for the displacement field can be associated with the thermal atomic vibrations in crystals [13].

First, we evaluate the total pair distribution function [14], $g(r)$,

$$g(r) = \frac{V}{N^2} \left\langle \sum_{i \neq i'} \delta(r - r_{ii'}) \right\rangle, \quad (1)$$

where $i \equiv (\mathbf{n}, j)$ is an atomic index, $r_{ii'} = |\mathbf{r}_{\mathbf{n}',j'} - \mathbf{r}_{\mathbf{n},j}|$ is the distance between atoms i and i' , V stands for the volume of the crystal containing N atoms and angular brackets mean configurational averaging. The pair distribution function is simply related to its cumulative function, $\tilde{N}(r)$, in the following fashion,

$$g(r) = \frac{1}{4\pi r^2} \frac{d\langle \tilde{N}(r) \rangle}{dr}, \quad (2)$$

where $\langle \tilde{N}(r) \rangle$ is the number of atoms within the sphere of radius r centred at one of the atoms (which is not included in counting) and averaged over all the atoms (being the centres of the spheres) in the system. The static structure factor measurable in scattering experiments is related to $g(r)$ according to

$$S(Q) = 1 + \frac{4\pi\rho_0}{Q} \int_0^\infty r [g(r) - 1] \sin(Qr) dr, \quad (3)$$

where $\rho_0 = N/V$ is the mean atomic concentration.

In order to calculate the pair distribution function for disordered lattices, we evaluate an auxiliary function $N(r, \mathbf{R})$ being the total number of atoms enclosed by a sphere of radius r centred at position given by \mathbf{R} [15–17],

$$N(r, \mathbf{R}) = \int_{|\mathbf{r}' - \mathbf{R}| \leq r} \rho(\mathbf{r}') d\mathbf{r}', \quad (4)$$

where

$$\rho(\mathbf{r}) = \left\langle \sum_{\mathbf{n},j} \delta(\mathbf{r} - \mathbf{r}_{\mathbf{n},j}) \right\rangle, \quad (5)$$

is the number density.

The evaluation of number of regular lattice points ($\sigma_j = 0$) within a sphere of radius r and its fluctuations around expected value is a known problem in the number theory [15–18] and a similar method can be used for disordered lattices. Applying the Poisson summation formula and evaluating Gaussian integrals we obtain,

$$N(r, \mathbf{r}_{\mathbf{n},j}^{(0)}) = \frac{4\pi r^3 \rho_0}{3} + \rho_0 \sum_{\mathbf{G} \neq 0} \left(\frac{2\pi r}{G} \right)^{3/2} J_{3/2}(Gr) \frac{1}{N_{\text{uc}}} \sum_{j'=1}^{N_{\text{uc}}} e^{-i\mathbf{G} \cdot \mathbf{R}_{j'} - G^2 \sigma_j^2 / 2}, \quad (6)$$

where \mathbf{G} are the reciprocal lattice vectors, $\mathbf{R}_{j'} = \mathbf{R}_j - \mathbf{R}_{j'}$, and $J_{3/2}(x)$ is the Bessel function. In the limiting case of a regular Bravais ($N_{\text{uc}} = 1$) lattice with $\sigma_j = 0$, this expression for $N(r, \mathbf{r}_{\mathbf{n},j}^{(0)})$ coincides with the known result [15–17]. Equation (6) is obtained for the number of disordered lattice points within the sphere centred at the regular lattice point $\mathbf{r}_{\mathbf{n},j}^{(0)}$. In order to obtain $\tilde{N}(r)$, used in the definition of $g(r)$ (see equation (2)), we place the origin of the sphere at the point coinciding with $\mathbf{r}_{\mathbf{n},j}$, average over this position and then subtract the contribution due to the atom displaced around $\mathbf{r}_{\mathbf{n},j}^{(0)}$. The resulting expression for $\tilde{N}(r)$ after averaging over the unit cell reads,

$$\begin{aligned} \tilde{N}(r) = & \frac{4\pi r^3 \rho_0}{3} + \rho_0 \sum_{\mathbf{G} \neq 0} \left(\frac{2\pi r}{G} \right)^{3/2} J_{3/2}(Gr) \frac{1}{N_{\text{uc}}^2} \sum_{jj'} e^{-i\mathbf{G} \cdot \mathbf{R}_{j'} - G^2 \sigma_j^2 / 2 - G^2 \sigma_j'^2 / 2} \\ & - \frac{1}{N_{\text{uc}}} \sum_j \left[\text{erf}(r/2\sigma_j) - \frac{r}{\sqrt{\pi}\sigma_j} e^{-(r/2\sigma_j)^2} \right], \end{aligned} \quad (7)$$

where $\text{erf}(x)$ is the error function. The last term in equation (7) accounts for the atom at the origin of the sphere not included in $\tilde{N}(r)$.

The pair distribution function is obtained from equation (7) by differentiation with respect to r according to equation (2),

$$\begin{aligned} g(r) = & 1 + \sum_{\mathbf{G} \neq 0} \frac{\sin(Gr)}{Gr} \frac{1}{N_{\text{uc}}^2} \sum_{jj'} e^{-i\mathbf{G} \cdot \mathbf{R}_{j'} - G^2 \sigma_j^2 / 2 - G^2 \sigma_j'^2 / 2} \\ & - \frac{1}{\rho_0 N_{\text{uc}}} \sum_j (4\pi \sigma_j^2)^{-3/2} e^{-(r/2\sigma_j)^2}. \end{aligned} \quad (8)$$

It follows from the above expression that the pair distribution function contains many oscillating components $\propto \sin(Gr)$ which decay according to a power law at large distances, i.e. $\propto 1/r$. For strongly disordered lattices, $G\sigma_j \gg 1$, all the oscillations corresponding to large magnitudes of the reciprocal lattice vectors are suppressed and only one component with minimal value of G survives. This explains the known singular frequency oscillations of $g(r)$ in strongly disordered regular lattices [7].

The static structure factor is the Fourier transform of $g(r)$ (see equation (3)), i.e.

$$S(Q) = 1 + \frac{2\pi^2 \rho_0}{Q^2} \sum_{jj'} e^{-G^2 \sigma_j^2 / 2 - G^2 \sigma_j'^2 / 2} \sum_{\mathbf{G} \neq 0} e^{-i\mathbf{G} \cdot \mathbf{R}_{j'}} \delta(Q - G) - \frac{1}{N_{\text{uc}}} \sum_j e^{-(Q\sigma_j)^2}, \quad (9)$$

which contains an analytic contribution due to diffuse scattering, $1 - N_{\text{uc}}^{-1} \sum_j e^{-(Q\sigma_j)^2}$, and a singular contribution from the δ -functional Bragg peaks with weighted intensities [13]. In the case of homogeneous displacement field, $\sigma_j = \sigma$, the static structure factor for disordered lattice can be expressed through the static structure factor of unperturbed lattice, $S_{\text{cryst}}(Q)$, as

$$S(Q) = 1 - e^{-(Q\sigma)^2} + e^{-(Q\sigma)^2} S_{\text{cryst}}(Q), \quad (10)$$

with

$$S_{\text{cryst}}(Q) = \frac{2\pi^2\rho_0}{Q^2} \sum_{\mathbf{G} \neq 0} \sum_{jj'} e^{-i\mathbf{G}\cdot\mathbf{R}_{jj'}} \delta(Q - G). \quad (11)$$

The last expression for $S_{\text{cryst}}(Q)$ can easily be obtained using the Poisson summation formula in the definition of $S(\mathbf{Q}) = N^{-1} \sum_{i,i'} e^{i\mathbf{Q}\cdot\mathbf{R}_{ii'}}$ and then performing orientational averaging over \mathbf{Q} directions. Equation (10) with Q replaced by \mathbf{Q} describes the effect of diffuse scattering by uncorrelated thermal-like atomic displacements and it is well-known in the diffraction theory [13]. However, its orientational averaging leading to equations (10) and (11) usually is not undertaken because it is irrelevant for crystals but certainly is necessary for isotropic glassy systems.

Equations (8) and (9) for the pair distribution function and static structure factor for disordered lattices are the main formulae which will be used in the following section for interpretation of the structural characteristics of topologically disordered systems. These expressions can be easily modified for different types of the displacement field in a similar manner to those derived in [19], and the anisotropy in atomic displacements can also be incorporated straightforwardly.

3. Pair distribution function for topologically disordered systems

In the previous section, we derived the expressions for the pair distribution function and static structure factor for positionally disordered lattices of any symmetry. The availability of analytical expressions for these characteristics gives us an advantage in understanding the features of these functions and suggests a possible use of them in the interpretation of similar characteristics for real disordered systems. However, an obvious disadvantage of $g(r)$ and $S(Q)$ given by equations (8) and (9) for such an interpretation comes from their quite different behaviour as compared to that for real glasses. For the pair correlation function, this difference is related to different decay laws at large distances, $r \rightarrow \infty$. Namely, the envelope of the pair distribution function for real glasses decays exponentially describing the damped density oscillations [8–10] in contrast to the power-law decay $\propto 1/r$ of $g(r)$ given by equation (8). This difference in decay law of $g(r)$ is reflected in the different shape of $S(Q)$ for disordered lattices and real glasses. For disordered lattices, the static structure factor is a set of δ -functions superimposed onto the continuous diffuse scattering contribution (see the thin solid line in figure 1). In glasses, the shape of $S(Q)$ can be imagined as a similar contribution from diffuse scattering and a superimposed contribution from broadened δ -functional peaks (cf the bold and thin lines in figure 1).

As seen from figure 1, the position of the first Bragg peak for c-Si coincides with position of the FSDP for a-Si. In many other materials, a similar correspondence between the FSDP and the first Bragg peak in disordered systems and their crystalline counterparts has been found [2, 7, 8, 10, 11, 23]. This leads us to a simple model which can be suggested as an explanation of the functional form of the static structure factor in disordered materials. The reciprocal lattice vectors, \mathbf{G} , are well defined in crystals due to the existence of the translational invariance in the system. In glasses, such an invariance is lost and the \mathbf{G} -vectors no longer exist. However, the presence of short-range order permits us to introduce pseudo-lattice (direct and reciprocal) vectors which now are complex values with imaginary part of the pseudo-lattice vector magnitude, G'' , describing a typical inverse length scale of exponential decay of the pair distribution function, and with the real part G' approximately coinciding with the magnitude of the reciprocal lattice vectors, $G' \simeq |\mathbf{G}|$. A similar approach is well-known in the theory of damped density oscillations in simple fluids [9, 24, 25]. In the Q -space, the use of complex

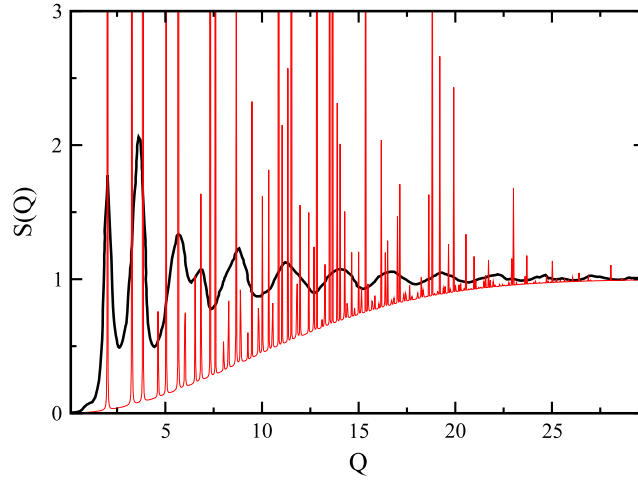


Figure 1. Static structure factor for amorphous Si (a-Si) (experimental data [20, 21] shown by bold solid line) and for positionally disordered crystalline Si (c-Si) (thin solid line) with $\sigma^2 = 0.0059 \text{ \AA}^2$ representing the mean squared displacement of Si atoms at $T = 293 \text{ K}$ [22].

reciprocal lattice vectors is equivalent to replacement of the δ -functional contributions by the Lorentzians, i.e.

$$\delta(Q - G) \rightarrow \frac{1}{\pi} \frac{G''}{(Q - G')^2 + (G'')^2}, \quad (12)$$

with G being replaced by complex value $G' + iG''$. The back Fourier transform of $S(Q)$ (see equation (9)) with $\delta(Q - G)$ replaced by Lorentzians results in exponentially decaying oscillating contributions with asymptotically surviving contribution characterized by the smallest G'' -value.

This simple heuristic argument (see equation (12)) allows the origin of the exponentially damped density oscillations and the shape of the static structure factor in topologically disordered systems to be explained. Namely, the shape of the static structure factor can be imagined as being obtained by the Lorentzian broadening of the δ -functional contributions in the corresponding crystalline counterpart. Consequently, the exponential decay of the pair distribution function is governed by the smallest value of the imaginary part of the pseudo-Bragg vectors in the crystalline counterpart.

In order to support the above model for the structural characteristics of topologically disordered solids, we present some numerical evidences for two typical amorphous structures, amorphous silicon (see figure 2) and vitreous silica, v-SiO₂ (see figure 3) below. In both cases, the following assumptions are made: (i) $G' = |\mathbf{G}|$ and (ii) $G'' = \lambda = \text{const}$. The first assumption signifies the fact that the position of the peaks for glassy $S(Q)$ mainly coincide (at least for small values of Q) with the location of the δ -functions for the corresponding crystalline static structure factor. The second assumption is rather simplistic and is related to the lack of knowledge of broadening factors (G'') (a similar conjecture has been made in [10]). This is due to the absence of a theory for the static structure factor in topologically disordered solids. Experimental data for $S(Q)$ provides the data only for the smallest value of G'' which is equal to the inverse exponential decay length of the pair distribution function or equivalently it coincides with the width of the FSDP. Typically (certainly, for a-Si and v-SiO₂), a single Bragg peak is the main contributor to the FSDP and thus the broadening for this peak can be measured experimentally. For higher- Q peaks the situation is more complicated because many

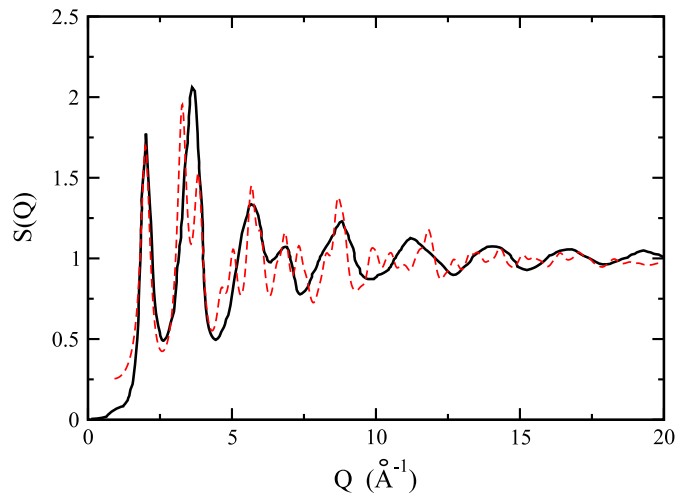


Figure 2. Static structure factor for amorphous silicon (experimental data [20, 21] shown by bold solid line) and for positionally disordered crystalline silicon (the dashed line) using the same value for σ_{Si}^2 as in figure 1, and a broadening factor $\lambda = 0.2 \text{ \AA}^{-1}$ which is consistent with experimental data [20, 21].

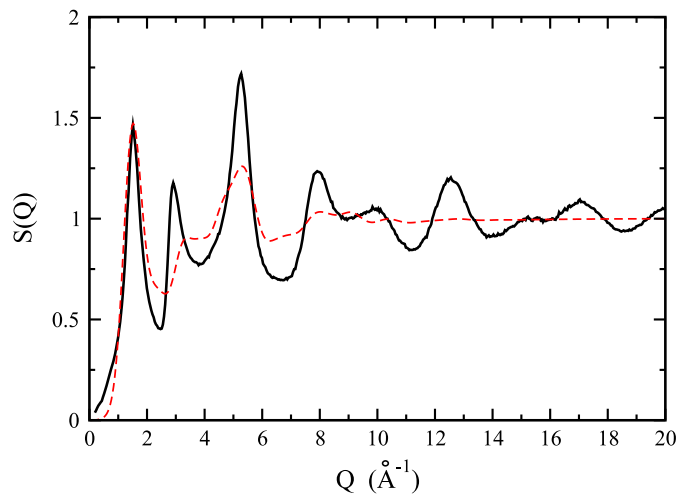


Figure 3. Static structure factor for vitreous silica (experimental data [26] shown by bold solid line) and for positionally disordered α -cristobalite (the dashed line) with $\sigma_{\text{Si}}^2 = 0.016 \text{ \AA}^2$ and $\sigma_{\text{Si}}^2/\sigma_{\text{O}}^2 = 0.6$ representing the mean squared displacements at $T = 300 \text{ K}$ (see [27] and references therein) and the broadening factor $\lambda = 0.3 \text{ \AA}^{-1}$ [10].

Bragg peaks can contribute to a single peak in the glassy structure factor (e.g. two Bragg peaks contribute to the second sharp diffraction peak in the case of a-Si; see figure 1) and evaluation of the broadening factors for these peaks is ambiguous. Therefore, aiming at quantitative agreement for the FSDP only, we assume that the broadening of all the Bragg peaks is the same and is equal to that for the FSDP. This very crude assumption can hardly lead to a reasonable agreement between the model and experimental data for static structure factor for Q -values above the FSDP.

As follows from figure 2, the FSDP in a-Si can indeed be well reproduced by Lorentzian broadening of the first Bragg peak in c-Si (cf solid and dashed lines in figure 2 in the range of the FSDP) which is formed by scattering from equally contributing planes {100}, {010}, {001} and {111} with $|\mathbf{G}| \simeq 2.0053 \text{ \AA}^{-1}$. The split between next two broadened Bragg peaks probably indicates that the broadening factors for them should be greater than for the first Bragg peak in order to reproduce the second sharp diffraction peak in $S(Q)$ for a-Si. A similar picture is demonstrated in figure 3 for v-SiO₂, where the FSDP is well reproduced by broadened Bragg peaks in α -cristobalite describing scattering from {101} and {011} planes with $|\mathbf{G}| \simeq 1.546 \text{ \AA}^{-1}$.

4. Conclusions

In conclusion, we have presented a simple model for the first sharp diffraction peak in topologically disordered solids. It is suggested that this peak originates from the first Bragg diffraction peak of the crystalline counterpart, which is broadened by a Lorentzian. The width of the Lorentzian is related to the imaginary part of the pseudo-Bragg vectors which replace the reciprocal crystalline lattice vectors. The model is supported by calculations of the static structure factor for a-Si and v-SiO₂ using the exact expression for $S(Q)$ in positionally disordered lattices.

The present model gives an additional support to the models of the FSDP based on pseudo-crystalline picture. In fact, it signifies the presence in glass of approximately identical structural units with the same local atomic order as in crystalline counterparts. These structural units (pseudo unit cells) influence atomic vibrational properties of glasses and result in the well-known pseudo-dispersion of disordered phonons [11, 23, 28]. Therefore, we believe that this simple model captures the main features of the FSDP and sheds light on its origin.

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