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## Hyperuniformity and static structure factor of amorphous silicon in the infinite-wavelength limit

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Abstract. The static structure factor of amorphous silicon (a-Si) models, containing 400,000 atoms with a density of 2.25  $g.cm^{-3}$ , has been studied by generating atomistic models using classical moleculardynamics simulations. The behavior of the structure factor, S(Q), in the limit  $Q \to 0$ , is examined to determine the degree of hyperuniformity in a-Si and is compared with the results with those from earlier simulations and small-angle X-ray scattering experiments. The study suggests that the computed value of the relative variance of the number of atoms at large distances, and hence  $S(Q \rightarrow 0)$ , lies in the range from 0.00736 to 0.00758, which is very close to the experimental value of 0.0076  $\pm$  0.0005, obtained from an extrapolation of transmission X-ray scattering data in the small-angle region. The non-zero value of the structure factor S(0) in *a*-Si can be attributed to density fluctuations on a very large length scale, which is a characteristic property of the structural and topological ordering of silicon atoms in the amorphous state.

#### **1. Introduction**

Amorphous silicon (a-Si) is an archetypal example of a non-crystalline semiconductor, which is characterized by the presence of short- and medium-range order on the length scale of 0–20 Å. Owing to its importance in technological applications [1], such as photovoltaics, thin-film transistors and liquidcrystal displays, the structural and electronic properties of a-Si have been studied extensively from experimental and computational points of view. The addition of a small quantity of hydrogen in a-Si improves its electronic properties, by passivating the dangling-bond defects (i.e., 3-fold coordinated atoms) present in the material. X-ray and neutron-diffraction measurements can be used very effectively in determining the structural properties of a-Si and its hydrogenated counterpart a-Si:H, respectively. Likewise, theoretical/computational efforts to study the structural and electronic properties of a-Si primarily focus on the development of suitable atomistic models and to analyze the resulting atomic distributions by examining the two- and three-body correlation functions. Since the static structure factor can be expressed as the Fourier transform of a two-body correlation function, namely the reduced pair-correlation function, one can directly compare the experimental structure factor with its simulated counterpart. While the structure factor alone cannot uniquely define a three-dimensional distribution of atoms, it is of particular interest in studying partially-ordered systems due to its ability to probe shortand medium-range order and its relationship with thermodynamic functions and kinetic coefficients [2]. In this communication, we address the behavior of the static structure factor, S(Q), of a-Si in the limit  $Q \to 0$ . The value of  $S(Q \to 0)$  furnishes information on the long-wavelength density fluctuations that are present in disordered/partially-ordered systems in the thermodynamic limit. For ordered systems,

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such as perfect crystals and quasicrystals, the static structure factor tends to zero as the wavevector (Q) approaches zero [3], and such systems are often referred to as hyperuniform systems [3–5]. In the following, we address this aspect of the static structure factor of *a*-Si in the infinite-wavelength limit and compare the results with those from small-angle X-ray scattering experiments and earlier simulations.

#### 2. Computational Method

Since the variation of structure factors in the small-angle region crucially depends on the distribution of atoms in real space at large distances, it is necessary to employ large models of a-Si to extract structural information from the reciprocal-space domain in the limit of the wavevector transfer  $Q \rightarrow 0$ . To this end, we have generated two ultra-large models of amorphous silicon, starting from random configurations, containing 400,000 Si atoms in a cubic box of length L=202.397 Å. The size of the models is significantly larger than the one used in an earlier simulation study by de Graff and Thorpe [6], who employed a 100,000-atom model of amorphous silicon, obtained from the modified WWW method of Barkema and Mousseau [7,8]. Unlike the WWW method, where an amorphous network is generated from a random network (in the modified WWW approach) or a crystalline diamond structure (in the original WWW approach) by employing a series of bond switches between neighboring atoms – followed by local/global relaxations of the resulting network – we have adopted a molecular-dynamical (MD) [9] route to produce structural models of amorphous silicon with a density of 2.25 g.cm<sup>-3</sup>. In a recent communication [9], we have shown that high-quality (i.e., low defect density) ultra-large models can be produced in MD simulations using the modified Stillinger-Weber potential [10] with a new cooling protocol. Once the configurations are generated and validated using experimental data, the structure factor, S(Q), can be obtained from the conventional pair-correlation function, q(r), which describes the radial correlation between a pair of atoms, separated by a distance r.

The computation of  $S(Q \rightarrow 0)$  for disordered/partially-ordered systems, from finite-size models, poses a nontrivial problem. For a homogeneous disordered systems, the structure factor can be obtained from the Fourier transform of the reduced pair-correlation function,  $G(r) = 4\pi\rho_0[g(r) - 1)]$ , where  $\rho_0$  is the average number density of the system, consisting of N atoms and a linear size of L. By taking angular averages, over all possible scattering directions, one can write,

$$S(Q) = 1 + \frac{1}{Q} \int_0^\infty G(r) \sin Qr \, dr \approx 1 + \frac{1}{Q} \int_0^{R_c} G(r) \, \sin Qr \, dr, \tag{1}$$

where the upper limit of the integral is truncated at  $R_c$  so that  $G(r \ge R_c) \approx 0$ . A choice of  $R_c \le \frac{L}{2}$  generally suffices to satisfy this condition. The limiting value of  $S(Q \to 0)$  now reads,

$$S(Q \to 0) \approx 1 + \int_0^{R_c} r G(r) \, dr. \tag{2}$$

While Eq. (2) provides an estimate of S(0), considerable difficulties appear in computing the integral accurately for large values of R before the upper limit  $R_c$  can be reached. On one hand, it is necessary to employ a sufficiently large model so that the limit  $Q(=\pi/L) \rightarrow 0$  is realized by incorporating radial correlations between pairs of atoms that are separated by large distances. On the other hand, the presence of small but finite numerical noise in G(r) is gravely magnified by the r term in r G(r) at large r, making the integral very sensitive to the upper limit,  $R_c$ . We shall see later that the presence of noise in rG(r) restricts the maximum value of  $R_c$  in a-Si to be of the order of 28–30 Å, depending on the system size and network quality. Thus, the usefulness of Eq. (2) is largely limited by the presence of noise in G(r) at large r, as noted by Levashov *et al.* [11]. An *ad hoc* approach would be to use an appropriate damping factor, such as an exponential or Gaussian function beyond a certain cutoff distance (in Eqs. (1) and (2)), to lessen the strength of the fluctuations with increasing radial distances and to extrapolate the value of S(0) in the limit  $Q \rightarrow 0$ . However, a physical basis for choosing such a damping factor needs to be established in

order to produce optimal results with few artifacts. The sampling-volume method, due to Torquato and Stillinger [5], provides a theoretical basis to construct an appropriate damping factor.

The determination of S(0) in the sampling-volume method [4, 5] relies on the observation that, in disordered or partially-ordered systems, the relative variance in the number of atoms (N) within a volume (V) is equivalent to the structure factor S(0) in the thermodynamic limit. This definition equally applies to perfectly-ordered systems and yields a value of S(0) = 0 in ideal crystalline and quasicrystalline structures. Such systems are known as hyperuniform systems and have been studied extensively by Torquato and coworkers [3, 5]. For amorphous silicon, a partially-ordered system, the relative variance of the number of atoms N(R), in a sample of volume V, where  $R \to \infty$ , is given by,

$$\lim_{R \to \infty} \frac{\langle N(R)^2 \rangle - \langle N(R) \rangle^2}{\langle N(R) \rangle} = S(0) = 1 + \int_0^\infty r \, G(r) \, \alpha(r; R) \, dr. \tag{3}$$

Here, the term  $\alpha(r; R)$  is proportional to the probability of finding two atoms, which are separated by a distance r, inside a randomly-placed sphere of radius R with N(R) atoms. Following Torquato and Stillinger [5], an expression for  $\alpha(r; R)$ , for a spherical volume of radius R in three dimensions, can be written as,

$$\alpha(r;R) = \begin{cases} \left(1 - \frac{r}{2R}\right)^2 \left(1 + \frac{r}{4R}\right) & \text{for} \quad r < 2R\\ 0 & \text{for} \quad r \ge 2R. \end{cases}$$
(4)

Equation 3 provides a better estimate of S(0) than Eq. (2), due to the presence of  $\alpha(r; R)$ , by reducing the artifacts that are associated with the fluctuations in rG(r) at large distances. It may be noted that the term  $r\alpha(r; R)$  in Eq. (3) is bounded above for a given value of R, which regularizes the value of the integral to a considerable extent.

#### **3. Results and Discussion**

In this section, we first validate the structural properties of the models, by analyzing the two- and threebody correlation functions, and then proceed to compare the computed values of S(0) with experimental data [12] and the results from earlier simulations [4, 6]. Hereafter, we will be using the term  $S(0^+)$  to indicate the use of finite-size models in this work. While we will be employing Eq. (3) to obtain the numerical value of  $S(0^+)$ , using the expression for the relative variance of the number of atoms and its integral representation, we shall also compute the approximated values of  $S(0^+, R_c)$  as a function of  $R_c$ in order to show the instability associated with computing  $S(0^+)$  from Eq. (2).

**Table 1.** Structural properties of 400,000-atom *a*-Si models: N, L,  $\rho$ ,  $C_4$ ,  $\langle r \rangle$ ,  $\theta$  and  $\sigma$  are the number of atoms, cubic box length, mass density, percentage of four-fold coordinated atoms, average bond length, average bond angle and RMS deviation of bond angles, respectively.

	N	L (Å)	$\rho~({\rm g.cm^{-3}})$	$C_4 (\%)$	$\langle r \rangle$ (Å)	$\theta$ (deg.)	$\sigma$ (deg.)
M1	400,000	202.397	2.25	97.6	2.386	109.2	9.73
M2		202.397	2.25	97.6	2.386	109.1	9.81

Figure 1(a) shows the reduced pair-correlation function (PCF) versus radial distances, averaged over M1 and M2 models. The reduced PCF shows a strong presence of radial correlations up to 15 Å, followed by a weak, lingering decay of up to 30 Å. Beyond 30 Å, it is difficult to distinguish the presence of radial correlations from numerical noise. The structure factor, S(Q), averaged over M1 and M2 models, is plotted in Fig. 1(b). The first sharp diffraction (FSDP) peak is correctly produced in the vicinity of 1.9

 $Å^{-1}$  and its height matches well with the experimental X-ray diffraction data from Laaziri *et al.* [13]. A structural analysis of the models reveals that the bond-angle distributions in M1 and M2 models are



**Figure 1.** (a) The reduced pair-correlation function (G(r)) of *a*-Si, averaged over M1 and M2 models, showing the persistence of oscillations up to at least 30 Å. The presence of noise in G(r), beyond 30 Å, is evident from the plot in the inset. (b) The average structure factor of *a*-Si obtained from the Fourier transform of the reduced PCF. Experimental X-ray diffraction data (red circles) from Ref. [12] are shown for a comparison.

both narrow and that they can be fitted with a Gaussian distribution  $N(\theta, \sigma^2)$ , where the average angle  $(\theta)$  and its RMS deviation  $(\sigma)$  are given by  $109.2^{\circ} \pm 9.73^{\circ}$  and  $109.1^{\circ} \pm 9.81^{\circ}$ , respectively. Likewise, an analysis of the coordination numbers of the atoms, with a nearest-neighbor cutoff distance of 2.7 Å, shows that 97.6% atoms are four-fold coordinated, while the remaining 2.4% atoms are equally distributed as three-fold coordinated atoms (1.2%) and five-fold coordinated atoms (1.2%) within the network. Table 1 lists the structural properties of M1 and M2 models.

Figures 2(a) shows the variation of the limiting values of  $S(Q \rightarrow 0)$ , obtained from Eq. (2), for different values of  $R_c$ . The following observations are now in order. First, the intense fluctuations in rG(r) produce considerable oscillations in the computed values of  $S(0^+, R_c)$  for  $R_c \leq 28$  Å, and the latter gets progressively worse beyond 30 Å due to the presence of noise in rG(r). Thus, an accurate determination of  $S(0^+)$  from Eq. (2), by incorporating distant radial correlations beyond 30–32 Å, is not feasible. Second, a more effective approach, in our view, is to fit the positive and negative amplitudes of  $S(0^+, R_c)$  in Fig. 2(a), in the region from 10 Å to 30 Å, and to obtain an average value of  $S(0^+, R_c)$  from the resulting fitted functions near 28-30 Å. It has been observed that the amplitudes of oscillations can be best fitted by an exponential function,  $a \exp(-\lambda x)$ , where the decay parameter  $\lambda$  is given by 0.114  $\pm$ 0.014 and 0.163  $\pm$  0.032 for the upper and lower fits in Fig. 2(a), respectively. This consideration leads to a value of  $S(0^+)$  that lies between 0.033 and 0.0279 in the region from 30 Å to 32 Å from the fitted functions. In contrast, the sample-volume method, with its integral representation of S(0), produces a considerably better estimate of  $S(0^+)$  for a spherical volume of radius R from Eq. (3). A comparison with Eq. (2) suggests that the presence of a non-zero sample-volume factor,  $\alpha(r; 2R)$ , for r < 2R, regularizes the integral to yield a value of  $S(0^+) \approx (7.363 \pm 1.711) \times 10^{-3}$  as  $R \to L/2$  in Fig. 2(b). Similarly, the relative variance (of the number of atoms) provides a stable and uniformly convergent value of  $S(0^+) \approx (7.58 \pm 0.19) \times 10^{-3}$  as R approaches L/2. In practice, it is necessary to restrict R well below L/2 so that a configuration-averaged value of the relative variance can be obtained by averaging over several sample volumes. Here, we choose a maximum value of  $R = L/2 - 2r_{Si} = 95$  Å, where  $r_{Si}$  is the radius ( $\approx 3.0$  Å) of the first coordination shell of Si atoms. Thus, the value(s) of  $S(0^+)$  obtained in our work is (are) comparable with the experimental value of  $S(0) = 0.0076 \pm 0.0005$ , extrapolated by Xie et al. [12], from highly accurate small-angle X-ray scattering data for annealed samples of a-Si.

#### 4. Conclusions

The static structure factor of a-Si has been studied, using atomistic models from ultra-large-scale molecular-dynamics simulations, to determine the value of S(Q) in the limit  $Q \rightarrow 0$ . The limiting



**Figure 2.** (a) The variation of  $S(0^+)$  with  $R_c$  from Eq. (2), averaged over M1 and M2 models. The amplitudes of the oscillations have been observed to follow an exponential decay. An estimate of  $S(0^+)$  can be obtained from the average-fit values (blue line) of the peak amplitudes near 28–30 Å. (b) The relative variance (blue diamonds) of the number of atoms, averaged over M1 and M2 models, in a spherical region of radius R, as  $R \to L/2$ , along with the corresponding values (red line) from Eq. (3).

value of  $S(Q \rightarrow 0)$  provides information on the long-wavelength density fluctuations that are present in a system in the thermodynamic limit. While the position and height of the first sharp diffraction peak in the structure factor (near 1.9 Å<sup>-1</sup> in *a*-Si) and its neighboring region characterize the presence of shortand medium-range order in partially-ordered systems, the value of  $S(0^+)$  is reflective of the degree of homogeneity or uniformity of the system in the infinite-wavelength limit. Together with the twoand three-body correlation functions, the value of S(0) provides a new figure of merit to characterize the structural quality of atomistic models on a very large length scale. Here, we have shown that the ultra-large atomistic models studied in this work not only produce the correct structure factor and bond-angle distribution, as observed by wide-angle X-ray diffraction, but also the value of  $S(0^+) \approx$ 0.00736–0.00758, which is very close to the experimental value of  $0.0076 \pm 0.0005$ , obtained from highly accurate small-angle transmission X-ray scattering measurements [12]. The values obtained in this work are considerably smaller than the earlier simulated value of  $0.035 \pm 0.001$ , reported by de Graff and Thorpe [6] using a 100,000-atom WWW model of *a*-Si.

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