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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 molecular-dynamics simulations. The behavior of the structure factor, $S(Q)$, in the limit $Q \rightarrow 0$, 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 ± 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 liquid-crystal 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 short- and 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 $Q \rightarrow 0$. The value of $S(Q \rightarrow 0)$ 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^{-3} . 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, $g(r)$, 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, $G(r) = 4\pi\rho_o[g(r) - 1]$, where ρ_o 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,

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

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

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

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 $rG(r)$ 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 distances. This observation is consistent with the intrinsic fluctuations of $G(r)$ 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 $R \rightarrow \infty$, is given by,

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

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,

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

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 three-body 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 , ρ , C_4 , $\langle r \rangle$, θ and σ 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)	ρ (g.cm ⁻³)	C_4 (%)	$\langle r \rangle$ (Å)	θ (deg.)	σ (deg.)
M1	400,000	202.397	2.25	97.6	2.386	109.2	9.73
M2	400,000	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

\AA^{-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

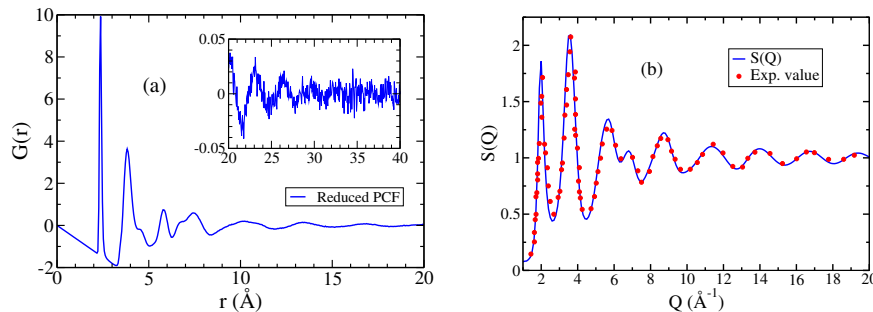


Figure 1. (a) The reduced pair-correlation function ($G(r)$) of a -Si, averaged over M1 and M2 models, showing the persistence of oscillations up to at least 30 \AA . The presence of noise in $G(r)$, beyond 30 \AA , is evident from the plot in the inset. (b) The average structure factor of a -Si obtained 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 $\mathbf{N}(\theta, \sigma^2)$, where the average angle (θ) and its RMS deviation (σ) 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 \AA , 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 $R_c \leq 28 \text{\AA}$, and the latter gets progressively worse beyond 30 \AA 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 \AA , 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 \AA to 30 \AA , and to obtain an average value of $S(0^+, R_c)$ from the resulting fitted functions near 28–30 \AA . 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 λ is given by 0.114 ± 0.014 and 0.163 ± 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 \AA to 32 \AA 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 $R \rightarrow L/2$ 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 $R = L/2 - 2r_{\text{Si}} = 95 \text{\AA}$, where r_{Si} is the radius ($\approx 3.0 \text{\AA}$) 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

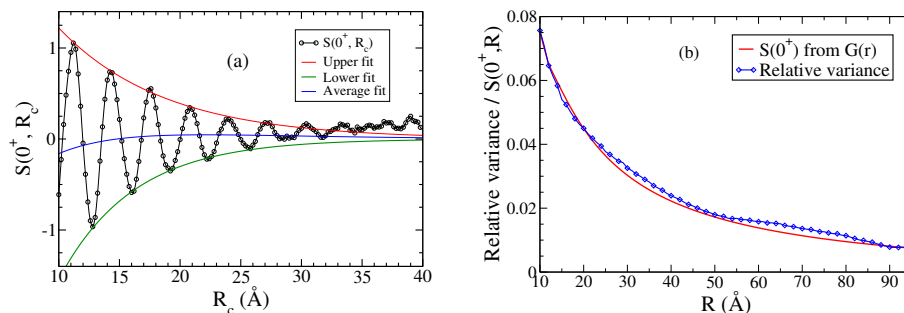


Figure 2. (a) The variation of $S(0^+)$ with R_c from Eq. (2), averaged over M1 and M2 models. The amplitudes of the oscillations have been observed to follow an exponential decay. An estimate of $S(0^+)$ can be obtained from the average-fit values (blue line) of the peak amplitudes near 28–30 Å. (b) The relative variance (blue diamonds) of the number of atoms, averaged over M1 and M2 models, in a spherical region of radius R , as $R \rightarrow L/2$, 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 \AA^{-1} in a -Si) and its neighboring region characterize the presence of short- and 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 two- and 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 $S(0^+) \approx 0.00736\text{--}0.00758$, which is very close to the experimental value of 0.0076 ± 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 ± 0.001 , reported by de Graff and Thorpe [6] using a 100,000-atom WWW model of a -Si.

Acknowledgments

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