Nearly-Hyperuniform Network Models of Amorphous Silicon

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We introduce the concept of *nearly hyperuniform network* (NHN) structures as alternatives to the conventional continuous random network (CRN) models for amorphous tetrahedrally-coordinated solids, such as amorphous silicon (a-Si). A hyperuniform solid has a structure factor $S(k)$ that approaches zero as the wavenumber $k \to 0$; we define a NHN as an amorphous network whose structure factor $S(k \to 0)$ is smaller than the liquid value at the melting temperature. Using a novel implementation of the Stillinger-Weber potential for the interatomic interactions, we show that the energy landscape for a spectrum of NHNs includes a sequence of local minima with an increasing degree of hyperuniformity (smaller $S(k \to 0)$) that correlates with other measurable features in $S(k)$ at intermediate and large k and with the width of the electronic band gap.

The development of accurate structural models of amorphous silicon (a-Si) and other tetrahedrally-coordinated solids has been an active area of research for the last eight decades [1–3], but many challenges remain. The structure of a-Si is approximated well by continuous random network (CRN) models [2, 3], the first of which was introduced by Zachariasen in 1932 [1]. Conventional CRNs for a-Si are fully four-coordinated, isotropic disordered networks that contain primarily five, six and seven atom rings, while maintaining nearly perfect local tetrahedral order (narrow bond-angle and bond-length distributions). Predictions derived from CRN models assuming a Keating potential describes the interatomic interactions are in good agreement with many structural properties of a-Si that are accessible via experiments, including the radial distribution function (RDF) and the phonon and electron density of states [3–5], nearest and next-nearest neighbors distances, bond statistics, ring statistics, etc. These successes are related to the form of the structure factor $S(k)$ at intermediate wavenumbers k.

In this Letter, we introduce the concept of *nearly-hyperuniform network* (NHN) structures and, on the basis of computer simulations, propose that NHN models may provide a better description of a-Si, especially after annealing. A perfectly *hyperuniform* solid has a structure factor $S(k)$ that approaches zero as the wavenumber $k \to 0$, implying that infinite- wavelength density fluctuations vanish [8]. The CRN models based on the Keating model that have been considered in the past (e.g., Ref. [4]) have values of $S(k \to 0)$ comparable to those found in the liquid phase at the equilibrium melting temperature, $S(k \to 0) \approx 0.03$. We define a *nearly* hyperuniform network as a disordered tetrahedral structure whose $S(k \to 0)$ is less than the liquid value at melting. As a practical matter, we shall be interested in cases where $S(k \to 0)$ is substantially less, by a factor of two or more.

Employing a novel simulation procedure that is based on the Stillinger- Weber (SW) potential to model the interatomic interactions, we generate a spectrum of NHN models and show that the energy landscape includes a sequence of progressively more hyperuniform minima with values $S(k \to 0)$ that are substantially less than the melting value – by a factor of two or more. We further show that the degree of hyperuniformity correlates with other measurable signatures in $S(k)$ at intermediate and large k and with the width of the electronic band gap. The simulations suggest that the sequence of states can be reached through extensive annealing, and more efficiently when combined with pressure. Companion experiments on a-Si will be reported elsewhere [6] that lend support to this picture.

While the SW potential has been shown to give a more realistic description of crystalline silicon [9], the energy penalty for dangling bonds is not sufficiently large, and hence quenches from the melt, via molecular dynamics, result in an unrealistic number of coordination defects. These defects are avoided in conventional CRN models by using the less realistic Keating potential that enforces perfect fourfold coordination.

In our study, we have devised a novel two-step numerical protocol to produce a spectrum of NHN models that combines the advantages of the Keating and SW potentials. Step one is a standard bond-switching annealing procedure using a Keating potential [10] applied to $20,000$ atoms within a cubic box (under periodic boundary conditions) [11] that is augmented with BM modifications [4]. However, unlike the BM CRN model, we anneal our systems significantly longer (between 2 to 250 times as long as measured by the number of accepted

transpositions) to achieve a sequence of inherent structures (local potential-energy minima) that have lower energies than those of the BM model. In the second step of our procedure, we use our end-state inherent- structure configurations obtained via a Keating potential (K1, K2, etc.) as *initial conditions* for atomic-position rearrangement under a modified SW potential [5, 12] at zero pressure via a conjugate gradient method. We label the corresponding inherent structures of this SW potential respectively SW1, SW2, etc. With this two-step procedure, the resulting structures possess a negligible number of dangling bonds; see Supplemental Material for additional simulation details, including structural and energy statistics for the resulting network configurations.

In Fig. 1, we show $S(0)$ as a function of the inverse of the height H of the first scattering peak in $S(k)$ for K (BM), the Barkema-Mousseau CRN model [7] as well as for K3, K5, SW3 and SW5 [13]. Importantly, it can be observed that K (BM) model is not an endpoint of annealing under the Keating potential, since further annealing produces a sequence K1 through K5 along a trajectory where $S(0)$ gets smaller and first peak height in $S(k)$ gets larger. Moreover, the models obtained by then quenching under the SW potential are nearly hyperuniform: they have values of $S(0)$ that are extend to more than 50% lower than their K progenitors and substantially below the value at the melting temperature. They also have substantially higher radial distribution function (RDF) first-peak heights (see Supplemental Material). The most nearly-hyperuniform structure obtained in our anneal run, K5, yields $S(0) = 0.010 \pm 0.002$, which is appreciably smaller than that of the BM model $[S(0) = 0.035 \pm 0.001]$ [7]. We note that we stopped with K5 because the annealing runs began to use unreasonable computational time; we believe that more refined hyperuniform amorphous networks are achievable with yet longer annealing times.

The SW5 model exhibits other signature features that correlate with increased hyperuniformity and can be measured experimentally:
(1) The SW5 structure possesses a bond-angle standard deviation that is more than a degree lower than that of the BM model and is in better agreement with recent bond-angle analysis of monatomic amorphous semiconductors [14]).
(2) The height of the first peak of $S(k)$ for the SW5 model is higher than for the BM model, as shown in Fig. 2(a) [15].
(3) The BM model has a significantly broader first peak in the RDF $g(r)$ (due to a larger bond-length variation) than the SW5, as shown in Fig. 2(b).
(4) For larger wavenumbers, the BM model predicts a significantly faster decay of the large-k oscillations in $S(k)$ than does that of the SW5 model [13], as shown in Fig. 3.
(5) Based on a simulations of smaller 1000-atom models and using a tight- binding model for silicon by Kwon [29],

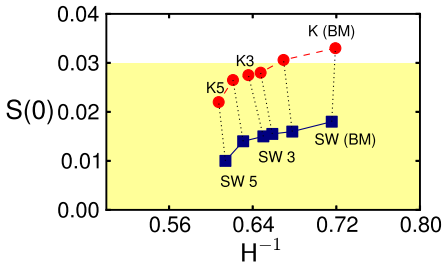

FIG. 1: $S(0)$ vs. the inverse height H of the first scattering peak for the K (BM) Keating annealed continuous random network model [7] and our Keating annealed models (circles) and the corresponding Stillinger-Weber quenched models (squares). The shaded region indicates the nearly hyperuniform range in which $S(k \to 0)$ is below the equilibrium melting value for a-Si; note that the SW models are substantially below this threshold.

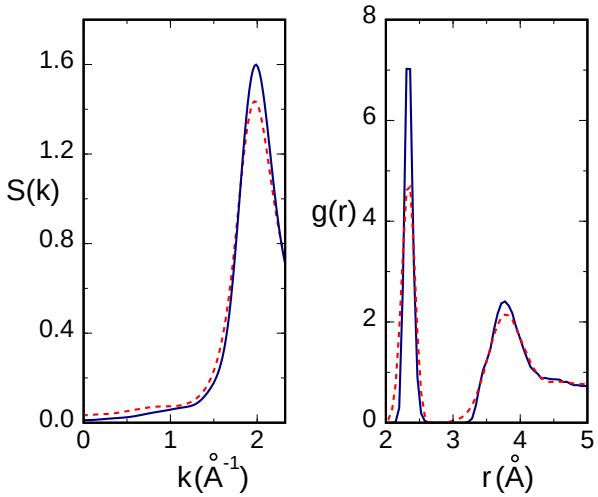

FIG. 2: (a) Comparison of the angularly averaged structure factor $S(k)$ versus k for small to intermediate k for the Stillinger-Weber quenched SW5 model (blue solid curve) and the Keating annealed K (BM) model [4] (red dashed line). (b) Comparison of the first peak in radial distribution function $g(r)$ versus radial distance r for the K (BM) model [4] (red dashed curve) and the SW5 model (blue solid curve).

the electronic band gap increases with increasing hyperuniformity, as shown in Fig. 4.

The fact that our annealing-quenching procedure produces a sequence of NHN models with an increasing degree of hyperuniformity (i.e., $S(0)$ tending to zero) has

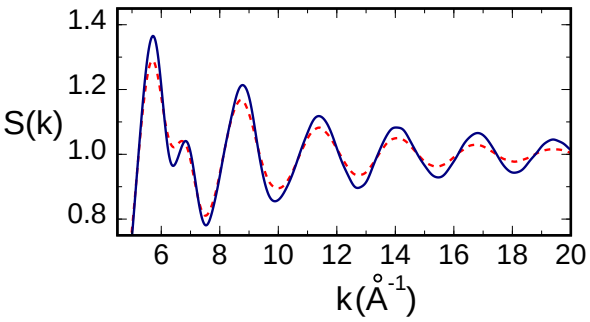

FIG. 3: The angularly averaged structure factor $S(k)$ versus k at large k for the Stillinger-Weber quenched SW5 model (blue solid curve) displays larger amplitude oscillations than the Keating-annealed K (BM) model [4] (red dashed curve).

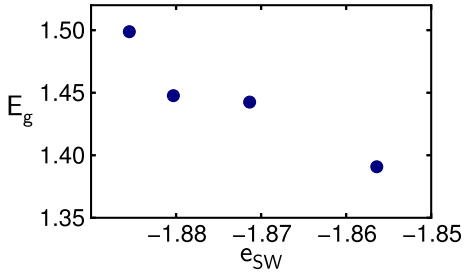

FIG. 4: Electronic band gap E_g vs. the average SW energy per atom e_{SW} (in units of $\varepsilon = 1.6483\,\mathrm{eV}$)

deep significance. First, it demonstrates that the energy landscape for conventional Keating-annealed CRN models, for Stillinger-Weber quenched models, and, hence, probably amorphous silicon has local minima that span a greater diversity of structures than was previously recognized and that, experimentally, it is possible to reach minima that are more nearly hyperuniform than had been thought achievable. In particular, the value of $S(0)$ cannot be considered a universal quantity for a-Si or any other amorphous tetrahedral network, as might be inferred from de Graff and Thorpe [7]. For example, while the percentage drop in the energy per atom in going from the K (BM) model to SW5 is about 23%, the corresponding drop in $S(0)$ is about 50%. Remarkably, the *configurational proximity metric* [17], which gauges the average local atomic movement required to transform one structure into another, is only about one percent of a bond-length with a corresponding percentage energy drop of only about 2.4% during our Stillinger-Weber (framework) quenching step from a Keating potential-annealed CRN to a SW potential-quenched NHN state, even though the latter possesses an $S(0)$ that is about one half the CRN value. This reveals the importance of collective atomic rearrangements during the second step of our quenching protocol.

Our findings are completely consistent with recent results for amorphous metals in which the atomic pair interactions are isotropic [18, 19]. In these studies, it has been demonstrated that, on approach to an inherent structure, $S(0)$ is nearly hyperuniform and decreases monotonically [18], and that $S(0)$ decreases as the temperature decreases. Also, deeper local minima in the energy landscape are accessed [19]. Thus, the observation that sampling deeper energy minima are accompanied by increased hyperuniformity appears to apply to a wide class of disordered systems (with both isotropic and directional interactions) and its full elucidation demands attention in the future.

Is it possible to construct a-Si with appreciably smaller $S(0)$ than reported here or, more ambitiously, reach true hyperuniformity ($S(k \to 0) = 0$)? There are both fundamental and practical reasons to consider such questions. On the practical side, our results above suggest that hyperuniform amorphous tetrahedral network models will have larger electronic band gaps than typical non-hyperuniform samples [2]. Similar ideas have successfully led to the creation of novel designer materials composed of a hyperuniform disordered arrangement of dielectric materials that have complete photonic band gaps [20–23]. On the theoretical side, our present computational results strongly indicate that continued annealing of a-Si samples improves the degree of hyperuniformity. Moreover, our simulations suggest that quenching a-Si samples under increased pressure leads to further decrease of $S(0)$ (see Supplemental Material for a table of dependence of $S(0)$ on compression).

Perfect hyperuniformity has been observed previously in disordered systems with hard, short-range isotropic interactions, most notably in a wide class of maximally random jammed packings [24, 25]. It has also been found in systems with soft, long range interactions; for example, in one component plasmas [26**?**] or in the ground states of so-called *stealthy* potentials [28] that enforce $S(k) = 0$ for a k in a range $[0, k_C]$, where $k_C > 0$. The existence of these diverse examples and our construction here of a sequence of increasingly hyperuniform configurations suggests that the search for a configuration with $S(k \to 0) = 0$ is one of the exciting areas for future research.

Even before our numerical studies of NHN models began, the general theoretical conjectures above stimulated recent measurements by Xie et al. [6] of the structure factor in the long-wavelength limit for a sample of a-Si synthesized by direct ion bombardment. These experiments have measured $S(k \to 0)$ to determine the degree of hyperuniformity both as-implanted and after annealing and have also checked several other correlated signatures pre-

dicted above. The results are reported elsewhere [6].

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