

## Properties of a Continuous-Random-Network Model for Amorphous Systems

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We use a Monte Carlo bond-switching method to study systematically the thermodynamic properties of a “continuous random network” model, the canonical model for such amorphous systems as  $a$ -Si and  $a$ -SiO<sub>2</sub>. Simulations show first-order “melting” into an amorphous state, and clear evidence for a glass transition in the supercooled liquid. The random-network model is also extended to study heterogeneous structures, such as the interface between amorphous and crystalline Si. [S0031-9007(98)07773-4]

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Amorphous materials have been intensely studied because of both their technological importance and fundamental interest. Because of the complexity of these systems, theoretical studies have relied mainly on numerical simulations. The standard method is molecular dynamics (MD) [1–4], where atoms are represented by point particles with more or less realistic interactions, and the equations of motion are integrated numerically.

Most studies of glassy behavior in amorphous systems have involved hard-sphere or Lennard-Jones models for metallic glasses. However, the most important and ubiquitous amorphous materials are network glasses such as  $a$ -SiO<sub>2</sub>. These may also be studied by MD, but large-scale or long-time simulations are limited to the few systems where suitable classical models are available for the atomic interactions [1,4]. Moreover, MD methods are inherently less efficient for strong network-forming materials, because there is a large energy barrier to breaking and reforming bonds in these systems. Most of the computer time is therefore spent in following local vibrations, waiting for the infrequent bond-switching events.

An alternative is to use the canonical model for such network glasses: a continuous random network (CRN) of atoms and bonds [5]. The most realistic available models of amorphous Si are of this type. They have been generated by Wooten, Winer, and Weaire [6] (hereafter WWW), using an ingenious Monte Carlo (MC) approach for generating random networks by bond switching.

In this paper, we extend this approach to study the thermodynamic properties of disordered materials. The system is represented explicitly as a CRN, i.e., as a set of atoms and a “neighbor list” specifying which pairs of atoms are connected by bonds. Equilibrium or quasi-equilibrium properties are determined by MC sampling, using the bond-switching move introduced by WWW.

The specific model system studied here has four bonds to each atom, as for  $a$ -Si. But we view it principally as a generic CNR model, and we systematically study its phase diagram and glass transition. This approach, and

the phase structure we find, should apply also to more complicated covalent amorphous solids such as  $a$ -SiO<sub>2</sub>.

In addition, this approach can be used to study the detailed properties of specific network systems, whenever an appropriate energy function is available. We illustrate this with a calculation of the interface between crystalline and amorphous phases of silicon.

We use a Keating-like valence force model [7] for the energy, which depends on both the positions  $\{\vec{r}_i\}$  of the atoms and the set  $\psi$  of bonds connecting pairs of atoms:

$$E_{\text{tot}}(\psi, \{\vec{r}_i\}) = \sum_{i,j \in \psi} \frac{1}{2} k_{\theta} b_0^2 (\cos \theta_{ij} - \cos \theta_0)^2 + \sum_{j \in \psi} \frac{1}{2} k_b (b_j - b_0)^2. \quad (1)$$

Here  $j$  represents the  $j$ th bond,  $b_j$  is its length,  $\theta_{ij}$  is the angle between bonds  $i$  and  $j$  connected to a common atom,  $b_0$  is the preferred bond length,  $\theta_0$  is the preferred bond angle, and  $k_{\theta}$  and  $k_b$  are “spring constants.” In order to focus on the role of network structure, we write the energy as a function solely of bond *topology*, minimizing  $E_{\text{tot}}$  with respect to the geometrical coordinates  $\{\vec{r}_i\}$ :

$$E(\psi) = \min_{\{\vec{r}_i\}} E_{\text{tot}}(\psi, \{\vec{r}_i\}). \quad (2)$$

Using  $E(\psi)$ , we can study the statistical properties of the system through MC simulation.

We use the WWW construction for the local MC moves in the  $\psi$  space. That is, from an initial configuration  $\psi_1$ , a bond is chosen randomly (call it  $BC$ ), and one more bond connected to each terminus is also chosen randomly (bonds  $BA$  and  $CD$ ). The only constraint is that all four atoms  $A$ ,  $B$ ,  $C$ , and  $D$  must be distinct. The switching move leading to  $\psi_2$  is then simply the cutting of bonds  $BA$  and  $CD$  and the formation of new bonds  $AC$  and  $BD$ . In this way the system samples topologically distinct configurations without introducing “dangling bonds” or changing the number of bonds to any atom.

It is important to emphasize the generality of this construction. Although it has been previously applied only to tetrahedral networks representing  $\alpha$ -Si, it is in fact equally applicable to any network. If there are two types of atoms with different coordination numbers, this move preserves the number of atoms with each coordination.

In systems with strong chemical order, such as  $\text{SiO}_2$ , the WWW move can be modified to preserve this order. This is done by choosing  $B$  and  $C$  as the (topologically) closest atoms of the same type, such as the two Si neighbors of an oxygen in  $\text{SiO}_2$ . Then  $A$  and  $D$  must be chosen similarly. We have studied the properties of  $\alpha$ - $\text{SiO}_2$  by using this extended WWW move.

For our purposes, these moves simply represent a means of sampling the space of configurations  $\psi$ . However, it is interesting to note that the actual dynamics of  $\alpha$ - $\text{SiO}_2$  and  $\alpha$ -Si may consist of precisely such moves [3,8].

For a given temperature  $T$ , one uses the Metropolis MC algorithm to decide whether a given switching move is accepted or rejected: the move is accepted with probability  $P = \min[1, \exp(-\Delta E/k_B T)]$ , where  $\Delta E = E(\psi_2) - E(\psi_1)$  is the energy change. Note that the temperature  $T$  applies only to the bond topology; the system is always in its ground state with respect to phonons. This makes the model less realistic in describing certain aspects of specific systems, but more generic in distilling the role of network topology and excluding other issues.

We choose parameter values appropriate for  $\alpha$ -Si:  $k_\theta = 0.647 \text{ eV/\AA}^2$ ,  $k_b = 9.08 \text{ eV/\AA}^2$ ,  $b_0 = 2.35 \text{ \AA}$ , and  $\theta_0 = 109^\circ$ . In addition, it is important that the neighbor list  $\psi$  remain consistent with the geometry  $\{\vec{r}_i\}$ , with close atoms included in the neighbor list, and distant atoms excluded. To guarantee this, we include an extra energy term  $E'$  in  $E_{\text{tot}}$  to prevent structures with “false” neighbors from occurring:  $E' = \gamma \sum_{mn} (d_2 - |\vec{r}_m - \vec{r}_n|)^3$ . Here  $m$  and  $n$  label atoms which are neither 1st nor 2nd neighbors in  $\psi$ , but for which  $|\vec{r}_m - \vec{r}_n|$  is actually less than the distance  $d_2 = 3.84 \text{ \AA}$  between next-nearest neighbors in crystalline silicon. We use  $\gamma = 0.5 \text{ eV/\AA}^3$ .

We begin our simulations with the diamond-structure crystal, where each atom has four bonds. At low  $T$  this crystalline phase is stable, while at high  $T$  the crystal “melts” into a disordered “liquid” phase. Note that this disordered system is still a network, with the same bond coordination as the crystal. Good glass formers such as  $\text{SiO}_2$  typically share this characteristic that the liquid retains the network structure [3].

It is difficult to determine the melting point accurately in a homogenous system, because of the energy barrier to nucleation of a new phase. We therefore create a system with a solid-liquid interface, and study the interface motion as a function of temperature. For temperatures  $T < T_m$ , the crystal phase will invade the amorphous phase, while for  $T > T_m$  the reverse occurs. The transition temperature  $T_m$  corresponds to the temperature where the interface motion vanishes.

The interface is prepared by allowing WWW switching in only half of the crystal cell, at sufficiently high  $T$ , this half becomes liquid. To determine the interface motion, the system is then cooled to the temperature of interest, and switching is allowed throughout the sample.

We have simulated interface motion in this manner at different temperatures for systems with  $N = 432$  atoms, with interfaces oriented along the  $[111]$  direction. Figure 1 shows snapshots of the atomic positions projected onto the  $(011)$  plane, at three successive times, for each of the two temperatures  $k_B T_1 = 0.50 \text{ eV}$  [Fig. 1(a)] and  $k_B T_2 = 0.55 \text{ eV}$  [Fig. 1(b)]. Figure 1 makes clear that the amorphous central region shrinks at temperature  $T_1$  by recrystallization, while at  $T_2$  the more stable amorphous phase grows at the expense of the crystal. We conclude that  $T_1 < T_m < T_2$ . From further calculations of this type, we estimate that  $k_B T_m \sim 0.53 \pm 0.01 \text{ eV}$ .

This  $T_m$  is a very high temperature, around 6000 K. Note that real Si does not form such a network liquid, but rather melts into a very different high-coordination liquid phase at much lower temperature, around 1700 K. In this respect, our model is more appropriate for good glass formers such as  $\text{SiO}_2$ , while real  $\alpha$ -Si can only be formed by processes which are very far from equilibrium.

We have also studied the properties of the homogeneous disordered network (the liquid phase) for temperatures both above and below  $T_m$ , for system size  $N = 216$ . In particular, the average energy per atom,  $E_a(T)$ , of the amorphous phase is determined by equilibrating for  $\sim 2 \times 10^5$  MC steps and then averaging over  $\sim 10^6$  MC steps, for each  $T$ . To further reduce inaccuracy due to statistical fluctuation, the result is averaged over typically

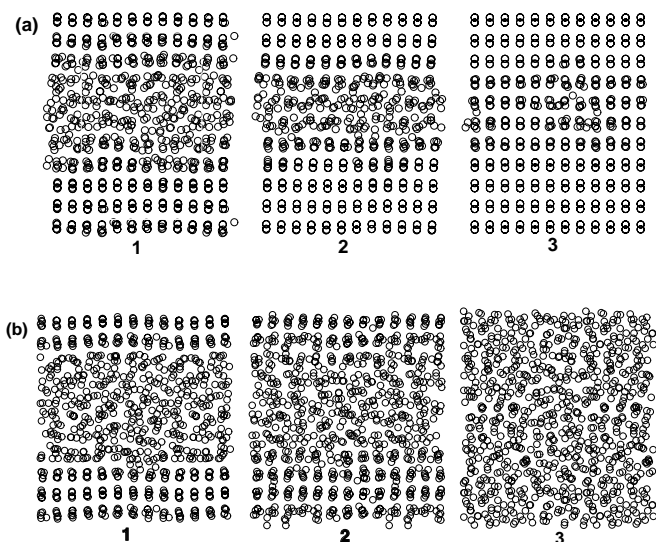


FIG. 1. Snapshots of projected atom positions at time intervals of 400 MC steps per atom. (a)  $T = 0.5 \text{ eV}/k_B$  ( $T < T_m$ ), where the crystalline phase eventually takes over the whole space. (b)  $T = 0.55 \text{ eV}/k_B$  ( $T > T_m$ ), where the whole system becomes amorphized.

10–20 runs with different random number seeds. From standard thermodynamic relations, we can then easily calculate the entropy,  $S_a(T)$ , and free energy,  $F_a(T)$ , per atom:  $S_a(T) = S_a(T_0) + \int_{T_0}^T (1/T)(\partial E_a/\partial T)dT$ , and  $F_a(T) = E_a(T) - TS_a(T)$ . It is particularly convenient to choose the arbitrary temperature  $T_0$  to be  $T_m$ , since  $F_a(T_m) = F_c(T_m)$ , where  $F_c(T_m)$  is the free energy for the crystal. In this model  $F_c(T) = 0$  to an excellent approximation for temperatures in the range of interest [9].

The resulting values for  $E_a(T)$ ,  $F_a(T)$ , and  $S_a(T)$  are shown in Fig. 2. When  $T < T_m$ ,  $F_a(T) > 0$ , so the crystal phase is thermodynamically preferred, while for  $T > T_m$ ,  $F_a(T) < 0$ , and the amorphous liquid phase is more stable. Our simulations clearly indicate that the crystalline phase is metastable in the region of stability of the amorphous phase, and vice versa, with a nucleation barrier separating the phases.

Thus, we are able to supercool the liquid and obtain well-defined quasiequilibrium properties for the metastable liquid below the first-order transition at  $T_m$ . The energy and entropy curves for this liquid exhibit fairly abrupt reproducible changes in slope at a rather well-defined temperature,  $k_B T_g \sim 0.4$  eV. This suggests that the liquid phase undergoes a glass transition at  $k_B T_g \sim 0.4$  eV ( $\sim 0.75 k_B T_m$ ), where it falls out of equilibrium even at our slowest cooling rate [10].

In the inset of Fig. 2, we show a cooling curve for the average energy of *a*-SiO<sub>2</sub> with cooling rate  $1.9 \times 10^{-5}$  eV per MC step. (To model SiO<sub>2</sub> we use the parameters of Ref. [11].) The transition (indicated by change of slope) is similar to that in the main figure, indicating the generality of this behavior.

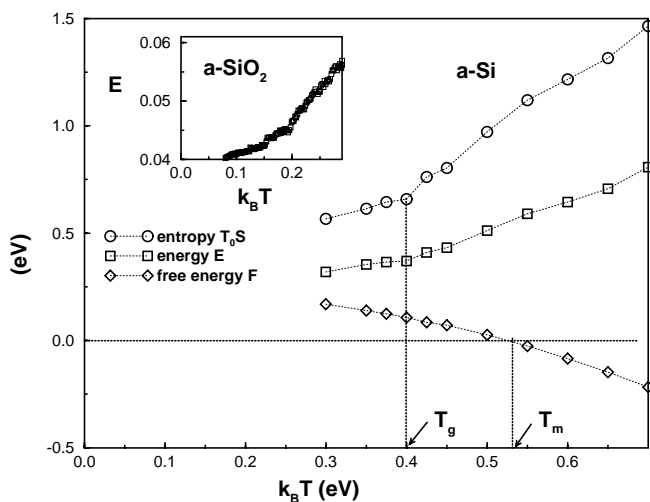


FIG. 2. Energy, entropy, and free energy per atom versus temperature for the amorphous phase averaged over 10–20 runs with statistical error about the size of the symbol. The break in slope for energy and entropy at  $T = T_g \sim 0.4$  eV/ $k_B$  corresponds to a glass transition. ( $T_0 \equiv 1$  eV/ $k_B$  is introduced so that entropy can be plotted in units of energy.) In the inset, a cooling curve for amorphous SiO<sub>2</sub> is shown for cooling rate  $1.9 \times 10^{-5}$  eV per MC steps.

It is interesting to note in Fig. 2 that extrapolations of  $E_a(T)$  and  $S_a(T)$  from above  $T_g$  would give negative values at very low temperature. This phenomenon is known as the Kauzmann paradox, and is rather common for materials that form structural glasses [12]. Of course there can be no true paradox, and the system does not follow the extrapolation. But this illustrates that our model reproduces the classic signatures of glassy behavior.

Figure 2 shows that the energy and entropy for  $k_B T < 0.4$  eV lie significantly above the curves extrapolated from higher  $T$ , thereby avoiding a true, unphysical paradox.

One can study this transition more quantitatively by calculating the “time”-dependent structure factor [13]

$$S(\vec{q}, t) = \langle \rho(\vec{q}, t') \rho(-\vec{q}, t + t') \rangle, \quad (3)$$

where  $\rho(\vec{q}, t')$  is the Fourier transform of the atomic density at time  $t'$ ,  $\rho(\vec{q}, t') = \sum_{j=1}^N \exp[i\vec{q} \cdot \vec{r}_j(t')]/\sqrt{N}$ , and the angle brackets denote an average over  $t'$ . In the liquid phase,  $S(\vec{q}, t)$  decays exponentially,  $S(\vec{q}, t) \sim \exp(-D|\vec{q}|^2 t)$ , where  $D$  is the diffusion constant of the liquid [14]. In a glass phase, however, the structure is frozen (albeit random), so  $S(\vec{q}, t)$  in the thermodynamic limit remains finite at long times. We choose  $|\vec{q}| = 2\pi/b_0$ , with  $b_0$  the bond length of the crystal structure, so that  $S(\vec{q}, t)$  will decay as rapidly as possible in the liquid phase. In addition to averaging over  $t'$ , we average over many orientations of  $\vec{q}$  to get better statistics. The results are shown in Fig. 3, where the normalized time-dependent structure factor  $S(|\vec{q}|, t)/S(|\vec{q}|, 0)$  is plotted versus time delay  $t$ , for four different temperatures around  $T_g$ . (The time units here are MC steps per atom.)

It can be seen from Fig. 3 that the structure factor decays to zero for  $k_B T = 0.40$  and  $0.45$  eV, but remains finite for the lower temperatures,  $k_B T = 0.30$  and  $0.35$  eV. Of course the number of accepted MC switching steps decreases with decreasing temperature. However,

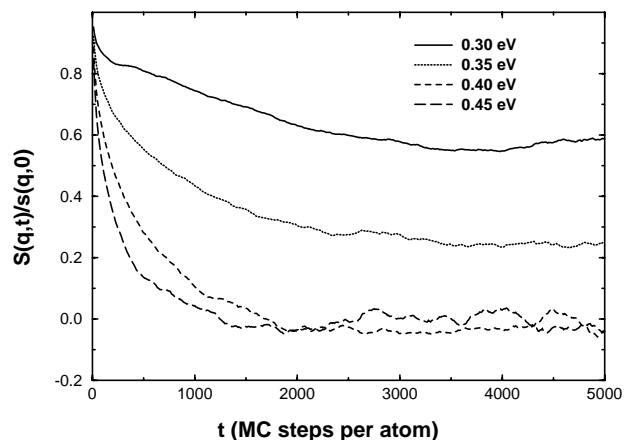


FIG. 3. Normalized dynamical structure factor versus time (in MC steps per atom) at wave number  $|\vec{q}| = 2\pi/b_0$  for temperatures around the glass transition.

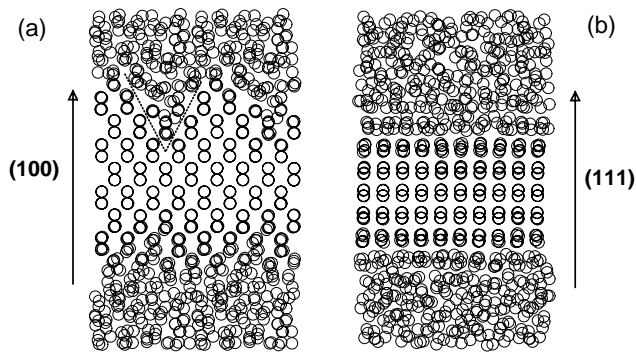


FIG. 4. Interface morphology for different orientations; (100) interface (a); (111) interface (b). The (100) interface develops (111) facets (dotted lines). The atom positions are projected onto the  $(01\bar{1})$  plane.

plotting the structure factor vs *accepted* steps gives a similar picture, leading to the same conclusion. The simulations ran long enough to produce more than 2000 *accepted* switching moves even for the lowest temperature,  $k_B T = 0.3$  eV.

These results confirm the conclusion above, that there is a well-defined glass transition in the idealized CRN model [10], and this transition occurs at  $k_B T_g \sim 0.40$  eV for the specific network considered here. Thus the CRN model has the following phase structure: In equilibrium, as temperature decreases there is a first-order transition from a disordered network liquid phase to the crystalline phase. The liquid phase may be supercooled below  $T_m$ , and at  $T = T_g < T_m$  undergoes a transition into a metastable glassy phase.

It is interesting to note that the model glass phase obtained by cooling the metastable liquid through  $T_g$  has essentially the same structure as was shown by WWW [6] to provide the best available model for the structure of real *a*-Si. Yet real *a*-Si is formed by radically different processes, very far from equilibrium. This suggests the existence of a rather well-defined metastable amorphous phase, whose structure (after annealing) is relatively independent of the kinetic history of the material.

As demonstrated in our calculation of  $T_m$ , the random network model can be adapted to study the interface between amorphous and crystalline phases. To investigate the effects of crystalline anisotropy, we prepared interfaces as before, oriented parallel to the (100), (110), and (111) planes of the crystal. We then equilibrated at  $T = T_m$ , the only temperature for which the interface is stationary. After initial transients, the (100) and (110) interfaces develop 111 facets, while the (111) interface remains flat. For the (100) interface, Fig. 4(a) shows the positions of all the Si atoms at one instant of time. It is clear that the interface is unstable — the dotted lines indicate two 111 facets which have formed. Similar faceting occurs for the (110) interface. Figure 4(b) shows that, in contrast, the (111) interface remains planar.

We can study the decay of crystalline order near the interface in the amorphous phase by calculating the local energy density, which is zero for the perfect crystal and nonzero in the amorphous phase. We find that the partial crystalline structure on the amorphous side of the interface always forms in double layers, consistent with the crystal structure in the [111] direction. This partial order decays rapidly away from the interface, with a decay length of roughly one (111) double layer.

In summary, we have studied the properties of a random-network model for amorphous materials. While we have used parameters for *a*-Si, the general behavior should be rather generic. We demonstrated the existence of a glass transition in an ideal network model. We have also applied the model to study the crystal-amorphous interface. For Si the (111) interface was found to be stable, but (110) and (001) interfaces are unstable against formation of (111) facets. This general approach should be applicable to a variety of systems which maintain a nearly ideal network structure, as well as for studies of generic aspects of network glasses.

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