Relaxed Continuous-Random-Network Models*

Paul Steinhardt† and Richard Alben
Department of Engineering and Applied Science, Yale University, New Haven, Connecticut 06520

M. G. Duffy and D. E. Polk
Allied Chemical Corporation, Materials Research Center, Morristown, New Jersey 07960

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Elastic-energy-relaxed 201-atom and 519-atom continuous-random-network structures are described, and $G(r)$'s, corrected for finite-size effects, are compared with experimental measurements on amorphous germanium. Excellent agreement is obtained for the principal peaks in $G(r)$. Even subtle features of $G(r)$ such as the shape of the second peak and structure between the second and third peaks accord remarkably well with experiment.

In a recent letter, Polk and Boudreaux[1] described a continuous-random-network model for which the positions of each model atom were measured and then nearest-neighbor distances were systematically equalized. Bond-angle deviations were not explicitly minimized and thus depend to some extent on the elastic properties of the plastic and metal units used to build the model.[2] In this comment we describe a procedure for simultaneously relaxing both bond-length and bond-angle distortions in continuous-random-network models. The procedure enabled us to rapidly build and obtain coordinates for a 201-atom model without measuring positions of atoms after the first 21. We also report results for the fully relaxed version of the 519-atom model of Ref. 1. The coordinates of the relaxed models depend on topology and on the assumed form for an elastic-distortion energy. They are completely unaffected by small changes in the assumed positions of the atoms before relaxation. The two fully relaxed models have quite similar features and agree remarkably well with experimental measurements of amorphous germanium.[3]

Coordinates for the continuous-random-network models of tetrahedrally coordinated atoms were obtained by a numerical procedure which minimizes the Keating[4] expression for the elastic energy:

$$V = \frac{3}{16}(\alpha/d^2)\sum_{l,i}(\vec{r}_{li}\cdot\vec{r}_{li}-d^2)^2 + \frac{3}{8}(\beta/d^2)\sum_{l(i,i')}(\vec{r}_{li}\cdot\vec{r}_{li'}+\tfrac{1}{3}d^2)^2, \quad (1)$$

where α and β are bond-stretching and bond-bending force constants, respectively; the first sum is on all atoms l and their four neighbors specified by i; the second sum is on all atoms and pairs of neighbors; and, $\vec{r}_{li}$ is the vector from l to its ith neighbor. The ratio β/α was taken as 0.2, which is in a range of plausible values indicated by phonon frequencies for diamond cubic silicon and germanium.[5,6]

According to the full-relaxation procedure, each atom, in turn, is moved toward the exact position of equilibrium under the bond-stretching and -bending forces due to its nearest and next-nearest neighbors. The identification of nearest-neighbor relationships must be specified in advance and is not altered by the procedure. Each repositioning of an atom requires a calculation of the forces on the atom and their derivatives, after which a simple matrix-inversion procedure gives the approximate equilibrium coordinates. The entire process for each atom is then cycled many times until equilibrium is achieved for all of the atoms. Provided the starting coordinates are not too far ($\lesssim \frac{1}{2}$ bond length) from equilibrium, angles and bond lengths converge to 1 part in 10^3 of their final values (determined by very long iterations) after 25 cycles for the models considered.

A combination of the full-relaxation procedure and a partial-relaxation procedure in which a central core of atoms was held fixed while added-on atoms were relaxed from automatically guessed start positions was used to build a 201-atom structure from a 21 atom rough-measured seed. The identification of nearest-neighbor relationships was made by referring to a hand-built representation of the structure. The hand-built model was built with plastic and metal units of the same type used by Polk.[1,2] A calculation of the amount of bond stretching and bending for each atom yielded a root-mean-square bond-length deviation of 0.80% and a root-mean-square angular deviation of 6.66°.

In order to create a second relaxed model, the 519 atoms in the enlarged Polk model were repositioned according to the full-relaxation program. For the original Polk network, in which the atoms were positioned so as to minimize the bond-length distortion, a root-mean-square bond-length deviation of 0.16% and a root-mean-square angular deviation of 9.25° over the entire model were measured. In comparison, for the relaxed 519-

atom model, an rms bond-length deviation of 1.04% and an rms angular deviation of 7.1° were found. Since the stored elastic energy of a structure is approximately proportional to the square of the rms angular deviation, the relaxation procedure accounts for nearly a 40% decrease in the total stored energy in the unrelaxed 519-atom model. If we take $\alpha = 0.387 \times 10^5$ dyn/cm for germanium,[7] the distortion energy of the 201-atom model is 19.7 meV/electron, that of the relaxed 519-atom model is 23.1 meV/electron, and that of the unrelaxed 519-atom model is 36.6 meV/electron.[6]

To calculate the density for each of the two models required a determination of the radius, r_0 (measured in bond lengths), of the largest sphere about the center of mass fitting inside the network which contained only fully bonded atoms. The average density as a function of radius was then plotted for radii from $r_0 - 1$ to $r_0 + 1$. From the asymptotic behavior of the plot and the random fluctuations in the curves, values for the density and the errors in those values were determined. Using for the average nearest-neighbor distance, the 2.45×10^{-8} cm found in crystalline Ge, densities of $(4.40 \pm 0.10) \times 10^{22}$ atoms/cm^3 for the 201-atom structure and $(4.41 \pm 0.06) \times 10^{22}$ atoms/cm^3 for the relaxed 519-atom structure were measured The diamond cubic density is 4.42×10^{22} atoms/cm.[3]

The radial distribution functions (RDF) [$J(r)$'s] for the models were found directly by forming a histogram of the distances between all pairs of atoms. In order to extract a meaningful pair distribution function and thus a $G(r)$, the $J(r)$'s were compared with that for a finite sphere of uniform density.[8] For such a sphere the average RDF is given by:

$$J_{\text{sph}}(r) = (N/a)\left[\tfrac{3}{16}(r/a)^5 - \tfrac{9}{4}(r/a)^3 + 3(r/a)^2\right], \quad (2)$$

where a is the radius of the sphere and N is the number of atoms.

For comparison with the two random-network models, the magnitude of a was adjusted so that the ratio of $J(r)$ to $J_{\text{sph}}(r)$ approached unity as the distance from the origin became large. The proper value for a was found to be 4.2 bond lengths for the 201-atom model and 5.7 bond lengths for the relaxed and unrelaxed 519-atom models. Given N, a, and the $J(r)$ for each model, we calculated a corrected $G(r)$ given by[9]

$$G(r) = [J(r) - J_{\text{sph}}(r)]/r, \quad (3)$$

and obtained the graphs in Fig. 1. When the atoms inside the largest sphere about the center of mass containing only fully bonded atoms were considered, only a slight sharpening in some of the details in $G(r)$ and an increase in statistical fluctuations occurred. We surmise from this that spurious effects from partially bonded surface atoms are not significant.

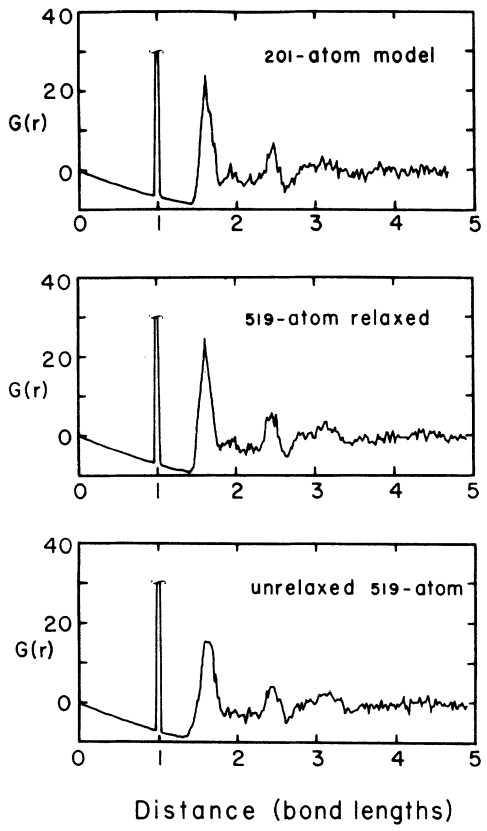

FIG. 1. Corrected $G(r)$'s for the 201-atom model and 519-atom relaxed model, both relaxed so as to minimize the Keating elastic energy with $\beta/\alpha = 0.2$, and for the unrelaxed 519-atom model as described in Ref. 1. The units of $G(r)$ are atoms/(bond length)^2. The curves are obtained by connecting the tops of histogram bars of width $\frac{1}{50}$th of a bond length. The first peaks are truncated for clarity of presentation.

An inspection of the three curves leads us to make two conclusions. First, relaxation of models through minimization of the Keating elastic energy brings about significant sharpening of features found in the $G(r)$ curves as may be seen by comparing the relaxed and unrelaxed curves for the 519-atom model in Fig. 1. Most obvious in this respect is the narrowing of the second-neighbor peak, a narrowing due to the decrease of 2.1° in the rms angular deviation after full relaxation. The relaxation also makes more visible the detail found between the second- and third-neighbor peaks in $G(r)$. Second, although the two models were constructed by different methods, they have in common all their prominent features and many subtler features, all of which are found in the data

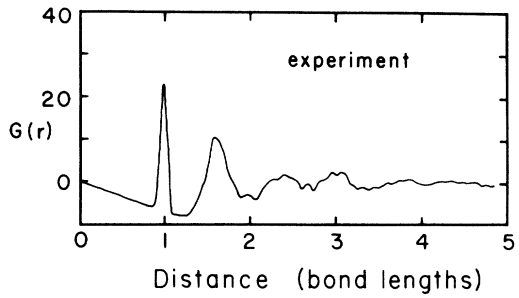

FIG. 2. Experimental $G(r)$ for sputtered amorphous germanium for Ref. 3. Units are the same as in Fig. 1, with the bond length taken as 2.45 Å.

reported by Graczyk and Chaudhari[3] from electron scattering in amorphous germanium (seeFig. 2). The positions of the four nearest-neighbor peaks in the two models agree to within 5% of the experimental values. The small peak in $G(r)$ between 1.9 and 2.0 bond lengths in the Graczyk data is evident in both of the relaxed models. Furthermore, the shoulders on the two sides of the second-neighbor peak in the experimental curves seem to be visible in both ramdom-network-model $G(r)$'s. Other characteristics not directly measured by experiment which the two models have been found to share are ring statistics and dihedralangle distributions. A more detailed analysis of the structures including ring statistics[10] will be published elsewhere.[11] Coordinates for the relaxed structures are available on request from the authors.

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†Present address: Department of Physics, California Institute of Technology, Pasadena, Calif. 91109.

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[9]This procedure differs slightly from that used by J. F. Graczyk and P. Chaudhari [Bull. Am. Phys. Soc. **18,** 420 (1973)] in their comparison of results for the unrelaxed 519-atom model with their measurements of amorphous germanium.

[10]The number of rings in the models, uncorrected for the effect of the surfaces, are as follows: for the 201-atom model, 49 fivefold, 100 sixfold, 102 sevenfold; for the 519-atom model, 137 fivefold, 308 sixfold, and 307 sevenfold rings. With corrections for surface effects, we estimate the bulk rings per atom ($\pm$ 10%) for both models as follows: 0.38 fivefold/atom, 0.90 sixfold/atom, and 1.05 sevenfold/atom.

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