Molecular dynamics simulations of a large structure of amorphous Si and direct calculations of the structure factor

LETTER TO THE EDITOR

Molecular dynamics simulations of a large structure of amorphous Si and direct calculations of the structure factor

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Abstract. There have been a number of simulations of fully bonded models of a-Si containing of the order of 10^2 atoms; comparison was then made with the pair distribution function deduced from neutron and x-ray scattering measurements on Si (or Ge). Obtaining the pair distribution function from the primary data produces a convoluted pair distribution function, and it seems sensible to compute the structure factor so as to make possible a direct comparison with experiment. We have taken the basic model of Wooten, Winer and Weaire and relaxed it slightly to conform to the Stillinger–Weber potential. This is a periodic structure but we have put together 64 such blocks, heated them rapidly to remove the periodicity, then cooled them rapidly to 0 K. The resulting structure factors agree extremely well with experimental measurements.

The understanding of many of the properties of amorphous materials is dependent on a knowledge of their structure. Information about the atomic order in such materials is usually a starting point for theoretical or numerical calculations of various phenomena such as the electronic properties. Available experimental data are often very limited and usually we only have information about the structure factor, which can be processed to yield the pair distribution of atoms albeit with some ambiguity in interpretation. It is clearly an ideal area for computer simulations where the amorphous structure generated in one way or another can be compared with various types of experimental data. In addition, it is extremely useful, from a theoretical point of view, to have 'ideal' structures without some of the features inevitably induced by particular methods of preparation.

The generation of amorphous structures has been performed in various ways. The most widely used model is one constructed by Wooten, Winer and Weaire (Wooten *et al* (1985), hereafter denoted as www). They constructed amorphous structures by starting from a crystalline material and performing stochastic atomic rearrangements. Another approach (CP), which is rather more fundamental, is that of Car and Parrinello (1988) based on a first-principles molecular dynamics technique using the lengthy total energy method. Another model (DFSD), also based on first-principles calculations, was put forward recently by Drabold *et al* (1990). A common feature of these models is the small size of the amorphous block of material. For www, CP and DFSD the number of atoms contained in a cubic cell was 216, 54 and 63 respectively. Even the biggest model

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(www) has a periodicity in the x, y, and z directions equal to only three lattice constants, namely 16.29 Å. Clearly the size of the models places constraints on the comparisons that can be made with real macroscopic solids. The importance of the size of a system was also stressed by Biswas *et al* (1987) when comparing the vibrational density of states for blocks containing 216 atoms and 512 atoms.

In all these models the comparison with experimental data is carried out using the radial distribution function (RDF). The RDF is very easy to obtain from computer models (but only up to distances equal to half the size of the box). On the other hand, the experimental RDF is calculated by Fourier transformation of a structure factor $S(q)$, which is obtained almost directly from experiments, and $S(q)$ is only available up to a maximum value q_{max} which is typically of the order of 15 Å^{-1}. Obtaining a RDF from the structure factor involves some slightly worrying features (see, for example, Etherington *et al* (1982) for critical comments) stemming from the fact that $S(q)$ is only available up to q_{max} and $S(q)$ may contain structure beyond q_{max}. The Fourier transform of $S(q) - 1$ multiplied by $\sin(\pi q/q_{max})/q$ yields a RDF that is convoluted in real space. Etherington *et al* (1982) make the comment that comparison between models and experimental results should always correspond to the same thing; that is, the models should be convoluted in the same way as the experimental RDFs.

It seems to us to be more straightforward to compare the experimental structure factor with the structure factor of a model. This value can be calculated directly if one has a model of reasonable size (the size of a model determines the density of available points in q-space). The structure factor also provides a better test of amorphization as was discussed by Wooten and Weaire (1986).

In this letter a method for generating the amorphous structure of silicon using molecular dynamics (MD) techniques is presented. Two features of our calculations differ from previous simulations. First the system size is much greater (13 824 atoms) corresponding to a box with periodic boundary conditions over a length of 65.59 Å. Secondly we compare our results with recent experimental data for the structure factor instead of the RDF. The comparison with an experimental structure factor was carried out by Luedtke and Landman (1989a) but they obtained the model $S(q)$ by Fourier transformation of the RDF. We are also able to make a comparison with data for Si, while only the scaled data for Ge were used by WWW and CP.

A standard MD technique was used with Andersen's (1980) method of constant pressure. The iteration time was equal 2.5×10^{-15} s and the 'piston mass' was set to 200 (in reduced units). The standard 'leap-frog' algorithm was used and we applied the Stillinger–Weber (SW) interatomic potential (Stillinger and Weber 1985) because of its relative simplicity. This potential is composed of a standard pair term and an additional three-body component stabilizing the tetrahedral network of silicon. This potential has been applied successfully to the simulations of a-Si by others (Broughton and Li 1987, Luedtke and Landman (1989a, b) and references therein) and to amorphous germanium by Ding and Andersen (1986).

In order to reduce the amount of computer time required for amorphization of the structure we used the WWW structure as a starting point. We first relaxed this structure using the SW potential. Only negligible displacements took place but the size of the box changed slightly; the equilibrium density of the block is 0.937 of that for crystalline silicon. We put together 64 such blocks forming a cube on which three-dimensional periodic boundary conditions (3D PBC) were imposed.

At this point we still had a structure with a 16.65 Å repeat distance. In order to get rid of this periodicity we annealed this block (with periodic boundary conditions in three

directions) for a very short time (1000 iterations steps at a temperature close to the melting point of Si (1600 K)). This choice of the temperature resulted from many tests we carried out. After heating, the structure was cooled down to 0 K and was allowed to relax. We are quite aware that such a heat treatment has nothing in common with real experimental methods of a-Si production; it is simply a way of generating an amorphous structure where there is no discernible remnant of the initial periodicity. The analysis of the influence of heat treatment on a structure is beyond the scope of this letter and will be published separately.

The structures were analysed by calculating the RDF and the structure factor. The RDF was obtained in a standard way by summation of the distances between atoms in the block, taking into consideration the 3D PBC. The structure factor is defined as (see, e.g., Allen and Tildesley 1989)

$$S(q) = \frac{1}{N} \sum_n \exp(i q \cdot R_n) \sum_n \exp(-i q \cdot R_n)$$

where R_n denotes the position of the nth atom and N the total number of atoms.

This quantity was calculated by a direct summation for a set of q_x, q_y and q_z chosen according to periodic boundary conditions, i.e. $q_x = 2\pi n_x/L$, $q_y = 2\pi n_y/L$, and $q_z = 2\pi n_z/L$ where L is a size of the box and n_x, n_y, n_z are integers. Because we are dealing with an isotropic system we calculated S as a function of the modulus q. The fluctuations in $S(q)$ provided us with a perfect test for the disappearance of the internal periodicity. If we put together some blocks we increase the number of available q-points but, as long as additional periodicity remains, the values of $S(q)$ at these additional points are equal (or close) to zero. Calculated in this way $S(q)$ contains, as is obvious, a lot of 'noise' corresponding to interference between waves from atoms separated by large distances. The experimental curves are smoother because of limited resolution, but in reality contain very rapid fluctuations which are not measurable. In order to facilitate comparison with experiment all our $S(q)$ curves were convoluted with a Gaussian with $\sigma = 0.1 \text{ Å}^{-1}$.

After many tests we found a more or less optimal computer heat treatment of the blocks. A short annealing at 1600 K followed by cooling down to 0 K was enough to get rid of the additional periodicity and quick enough to prevent the system from melting. If we define the coordination in terms the distance corresponding to the first minimum in the RDF (3.05 Å) the average coordination for our sample is equal almost exactly to 4 (for an ideal Si crystal and for the WWW structure it exactly equals 4). However, unlike in an ideal crystal and WWW structure there are coordination defects in our system. About 3% of the atoms have three nearest neighbours (NN) and about 3% of the atoms have five NN.

In figures 1 and 2 we present the comparison of the $S(q)$ for our system with very recent experimental data for a-Si (Fortner and Lannin 1989) (figure 1) and with experimental data for amorphous germanium (Etherington *et al* 1982) scaled for Si (figure 2; these data have often been used for silicon models). Figure 3 contains $S(q)$ calculated by us for a WWW structure using the same smoothing method. In figure 4 we plot the RDF for our model. This curve was obtained by direct summation of the number pairs within a bin width of 0.01 of a lattice constant. We have calculated the RDF $g(r)$ up to 33 Å but it is very close to unity for $r > 12$ Å.

It can be seen in figures 1 and 2 that the agreement between our curve and the experimental one is very good. All features of the experimental curves are present in
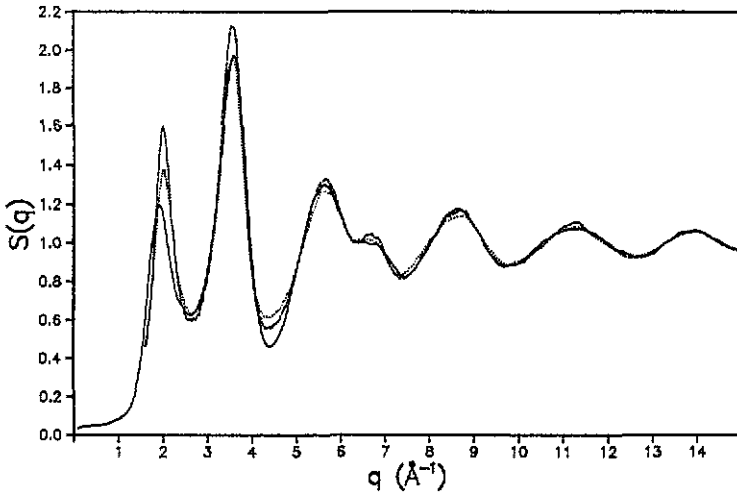
Figure 1. Comparison of $S(q)$ for our model (full curve) with results obtained by Fortner and Lannin (1989). The dotted curve corresponds to an 'as-deposited' film and the broken one to a film annealed at 600 °C for 1 h.
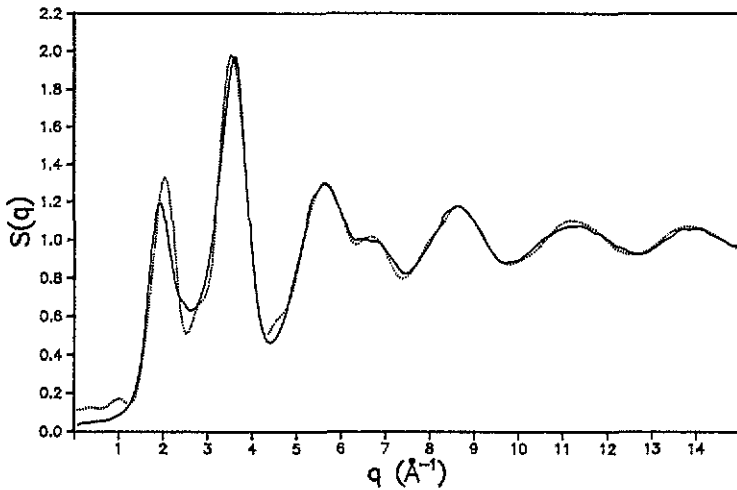

Figure 2. Comparison of $S(q)$ for our model (full curve) with that obtained by Etherington *et al* (1982) for Ge and scaled to represent Si (dotted curve).

our curve and the amplitudes agree quite well. When comparing our model with that of WWW (figure 3) it is obvious that our $S(q)$ curve is much smoother.

In this letter we have presented a method for generating the biggest amorphous model of Si, as far as we know. Periodic boundary conditions had to be applied but the length of this artificial periodicity is equal 65.59 Å. We believe that this model can be regarded as a true model of an amorphous system.
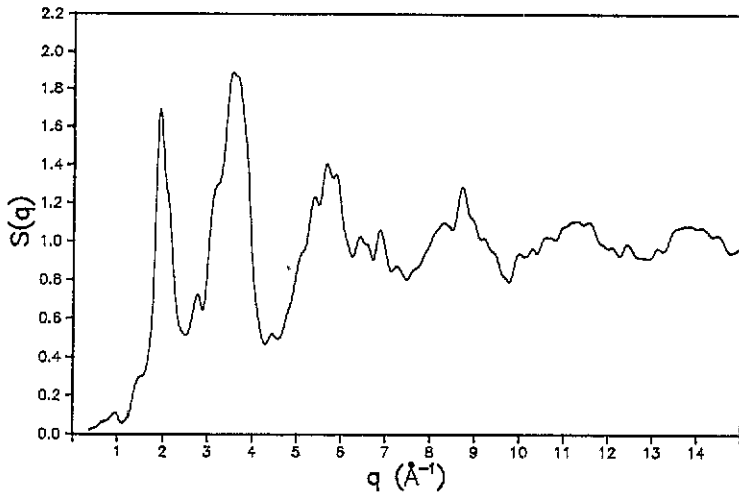
Figure 3. The structure factor $S(q)$ for the www model obtained using the same convolution function as for our model in figures 1 and 2.
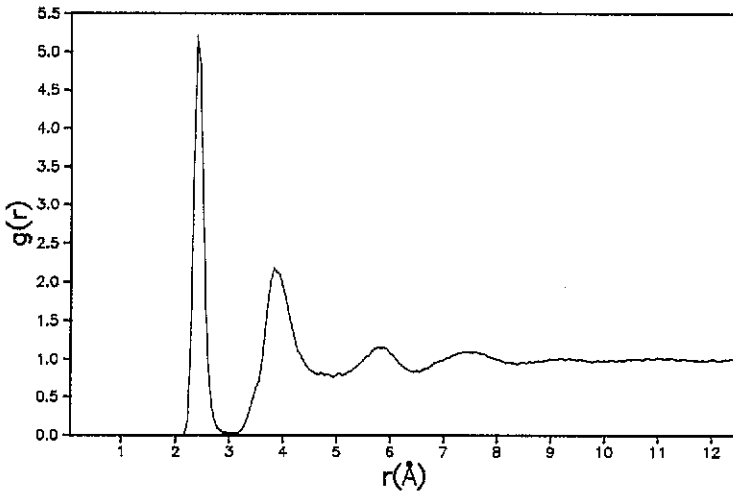

Figure 4. The RDF for our model (for $r > 12$ Å it is very close to unity).

Unlike other researchers, we have carried out the comparison with experimental data directly using the the structure factor, avoiding in this way the Fourier transformation of experimental data.

The Stillinger–Weber potential has been used in our study. We are quite aware of its limitations but we believe that its application for a bulk system is quite justified (there are many objections against using it for surface properties), and there are many other studies supporting its applicability for amorphous systems.

It is obvious that, becaue of the limitation on computer resources available at present, one has to chose between simulating a small (tens of atoms) system with very accurate

interactions (CP, DFSD) or simulating a very big system (thousands of atoms) using phenomenological potentials, as has been done in this letter. We are quite convinced that when dealing with disordered systems (liquids or amorphous materials) the latter is the more reasonable solution.

Simulations of an even bigger system (more than 100 000 atoms) are in progress and will be published soon, together with further analysis (energy, defects, thermal behaviour, influence of various 'thermal treatments') of the structure. We are also applying our structure in computer calculations of electronic properties of a-Si which will be published separately.

References

Allen M P and Tildesley D J 1989 *Computer Simulations of Liquids* (Oxford: Oxford Science Publications)
Andersen H C 1980 *J. Chem. Phys.* **72** 2384
Biswas R, Grest G S and Soukoulis C M 1987 *Phys. Rev.* B **36** 7437
Broughton J Q and Li X P 1987 *Phys. Rev.* B **35** 9120
Car R and Parrinello M 1988 *Phys. Rev. Lett.* **60** 204
Ding K and Andersen H C 1986 *Phys. Rev.* B **34** 6987
Drabold D A, Fedders P A, Sankey O F and Dow J D 1990 *Phys. Rev.* B **42** 5135
Etherington J H, Wright A O, Wenzel J T, Dore J C, Clarke J H and Sinclair R N 1982 *J. Non-Cryst. Solids*
    48 265
Fortner J and Lannin J S 1989 *Phys. Rev.* B **39** 5527
Luedtke W D and Landman U 1989a *Phys. Rev.* B **40** 1164
—— 1989b *Phys. Rev.* B **40** 11733
Stillinger F H and Weber T A 1985 *Phys. Rev.* B **31** 5262
Wooten F and Weaire D 1986 *J. Phys. C: Solid State Phys.* **19** L411
Wooten F, Winer K and Weaire D 1985 *Phys. Rev. Lett.* **54** 1392