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The bulk modulus of covalent random networks

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Abstract. We re-examine the calculation of the bulk modulus of random networks with a variable mean coordination $\langle r \rangle$ that ranges from $\langle r \rangle = 4$ down through the phase transition from rigid to floppy that occurs at around $\langle r \rangle = 2.4$. In contrast to previous workers, we use random-network models, rather than depleted diamond lattices, so our results are more relevant to glasses. We find that the bulk modulus behaves in a very similar way to that found previously for depleted diamond lattices, with the bulk modulus going to zero at around $\langle r \rangle = 2.4$ with an exponent of 1.4. In the course of this study we came across many examples of transitions between different local minima, especially in networks with a low mean coordination. We discuss and illustrate the nature of these metastable states and show that although there are differences in the local minimum *energy* associated with these states, the *bulk modulus* (curvature around the minimum) is essentially independent of which minima the system is in. We show that these nearly degenerate local minima are associated with different local configurations of very short polymer chains.

1. Introduction

It has been suggested by Phillips (1982) and by Thorpe (1983) that the elastic properties of random networks depend primarily on a single variable $\langle r \rangle$: the mean atomic coordination. Thorpe (1983) has predicted that a random covalent network is *rigid* for $\langle r \rangle > 2.4$, and *floppy* for $\langle r \rangle < 2.4$.

To gain an insight into the elastic properties of glasses, He and Thorpe (1985) performed a series of numerical simulations on computer-generated random networks. They calculated the elastic moduli, c_{11} , c_{44} , and bulk modulus B , for a series of random networks with varying mean coordination. These physical quantities couple very directly to the rigidity phase transition. To build a large number of random networks, He and Thorpe utilized a bond dilution of the *crystalline* diamond lattice. They started from a 512-atom crystalline diamond supercell that has $\langle r \rangle = 4$. The atoms interact via the Keating potential (1) (Keating 1966), with $\beta/\alpha = 0.2$:

$$V = \frac{3}{16} \frac{\alpha}{r_0^2} \sum_{l,i} (\mathbf{r}_{li} \cdot \mathbf{r}_{li} - r_0^2)^2 + \frac{3}{8} \frac{\beta}{r_0^2} \sum_{l\{i,i'\}} \left(\mathbf{r}_{li} \cdot \mathbf{r}_{li'} + \frac{1}{3} r_0^2 \right)^2. \quad (1)$$

Here the α -term is associated with bond stretching and the β -term is associated with bond bending, and i and i' are neighbouring sites of the reference atom at l . Bonds were removed in a random manner, maintaining the structure with periodic boundary conditions. When a bond was removed, *all* of the α - and β -terms involving that bond were also removed from the Keating potential. No dangling bonds were permitted, so an arbitrary atom can

have 2, 3 or 4 bonds. No other possibilities were allowed. After a certain number of bonds were removed at random, the structure was relaxed using the Keating potential. The initial crystalline structure, which served as a kind of reservoir of bonds, was a stress-free network. In this way a sequence of random networks was obtained over the whole range of allowed mean coordinations. For each mean coordination, three samples were generated with different statistics, by using three different random-number generators. Also, one of these three samples had an enhanced number of twofold-coordinated atoms at the expense of threefold sites. This served to validate the general prediction that the properties of the network depend mainly on $\langle r \rangle$ and not on other parameters.

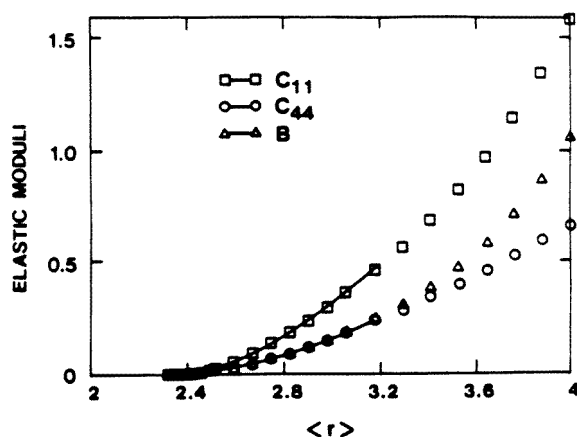


Figure 1. Elastic moduli averaged over three different samples as a function of the mean coordination $\langle r \rangle$ for $\beta/\alpha = 0.2$. These results are for bond-depleted diamond lattices as described in the text. Solid lines are power-law-fit curves (from He and Thorpe 1985).

The computed f dropped linearly to zero at $\langle r \rangle = 2.4$, as predicted by the mean-field theory, but it has a small tail at around the mean-field transition point. The elastic constants c_{11} and c_{44} , and the bulk modulus $B = \frac{1}{3}(c_{11} + 2c_{12})$, were computed using standard techniques (Feng *et al* 1985, Feng and Sen 1984). The 512-atom supercell was redefined in terms of an external strain ϵ , and the elastic moduli c were obtained from the elastic energy $\frac{1}{2}c\epsilon^2$ after the network had been fully relaxed. The results of He and Thorpe (1985) are shown in figure 1. He and Thorpe made a least-squares fit to the computed data and found that, within the range $2.4 < \langle r \rangle < 3.2$, all three elastic constants were very well approximated by the power law of the form (see figure 1)

$$c = \text{constant} \times (\langle r \rangle - 2.4)^{1.5}. \quad (2)$$

Equation (2) did not fit the data well at larger values of $\langle r \rangle$.

More recently, Franzblau and Tersoff (1992) performed computer simulations similar to those of He and Thorpe (1985) to calculate the elastic constants of random networks. They employed a direct algebraic approach in calculating the elastic constants (Franzblau and Tersoff 1992). Their model has only 216 atoms, but all results were obtained with the force-constant ratio $\gamma_c \equiv \beta/\alpha$ ranging over four orders of magnitude. These authors also use the same method of bond depletion of a crystalline diamond lattice as used by He and Thorpe (1985). The graphical results they present are for $\gamma_c = 0.655$ which is a value appropriate for diamond. This value of γ_c was a significantly larger value than the one used in work of He and Thorpe which was $\gamma_c = 0.2$ (appropriate to silicon or germanium).

Franzblau and Tersoff found that for this *particular value* of $\gamma_c = 0.655$, all three elastic constants (c_{11} , c_{44} , and the other shear constant $c_s \equiv (c_{11} - c_{12})/2$) follow a power law for the whole range of $\langle r \rangle$:

$$c = \text{constant} \times (\langle r \rangle - 2.394)^{1.40}. \quad (3)$$

In particular the elastic constant c_{44} follows a power law for the whole range of the parameter γ_c that was studied:

$$10\gamma_c < \gamma < \gamma_c/1000. \quad (4)$$

The exponent in the power law (3) varied from 1.35 to 1.89 within the range of γ_c studied. The other elastic constants exhibit more complex behaviour, and in general do not follow a power law over the whole range of $\langle r \rangle$, but only do so in the vicinity of $\langle r \rangle = 2.4$.

Note that the results of Franzblau and Tersoff (1992) are consistent with earlier results of He and Thorpe (1985) which were for a smaller value of $\gamma_c = 0.2$. According to Franzblau and Tersoff, c_{11} deviates significantly from the power law for small γ_c , and so it is not surprising that He and Thorpe (1985) were not able to fit the c_{11} - and B -constants for the whole range of $\langle r \rangle$ with a power law.

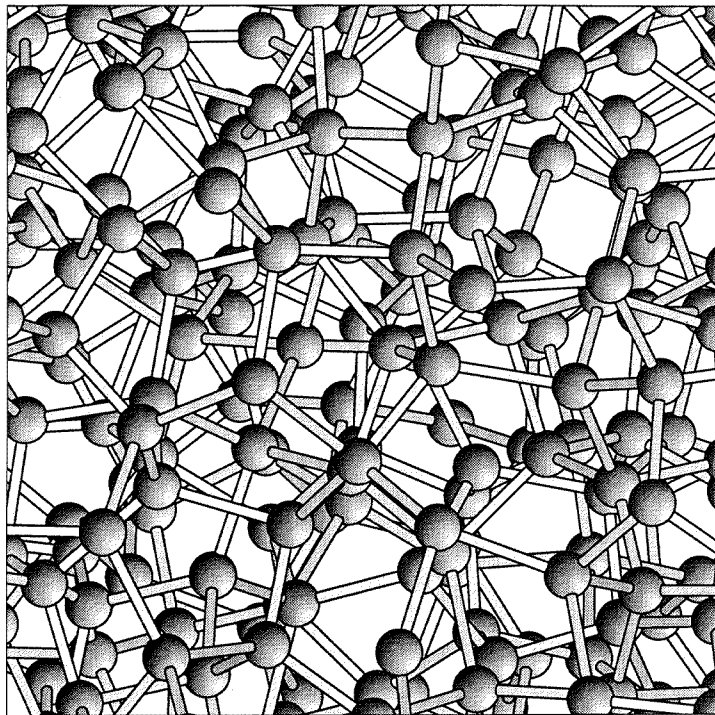


Figure 2. A piece of the amorphous diamond structure, previously obtained (Djordjević *et al* 1995) and used here as the underlying structure for bond depletion.

The layout of the paper is as follows. In the next section, we describe the construction of the depleted *amorphous* diamond network and its subsequent relaxation. We then examine the behaviour of the energy and the bulk modulus. Finally, we give an extended discussion of the nature of the metastable states.

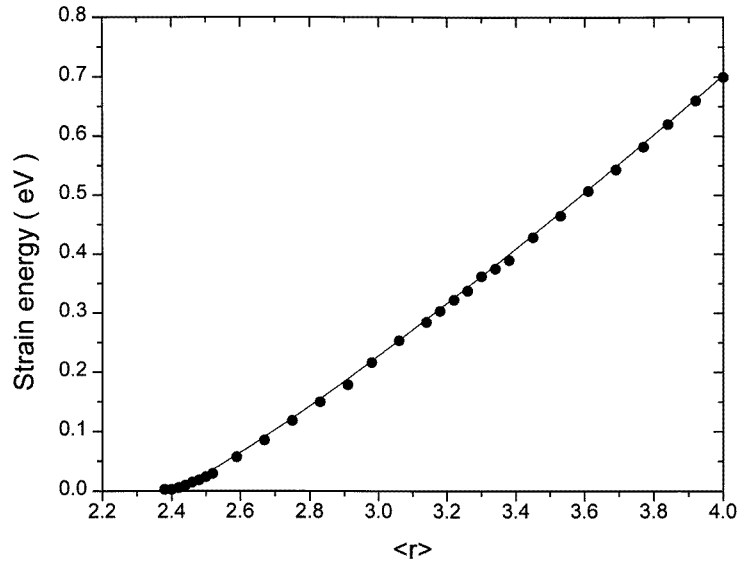


Figure 3. Dots represent the total strain energy averaged over 10 different configurations, as a function of the mean coordination $\langle r \rangle$. The solid line is the best-fit power-law curve, obtained using equation (2) with an exponent of 1.15. The energy is given in eV per atom.

2. Network construction and relaxation

As we have reviewed in the previous section, computer simulations of the elastic properties of random networks have been performed using a crystalline lattice as the underlying structure. In other words, the crystalline lattice is transformed into a random network by removing a certain number of bonds at random. One should be very careful in creating models of amorphous materials to avoid any crystalline memory in the final random network. Thus, one can be suspicious about the true *amorphousness* of the random network obtained by the random removal of bonds from an ideal crystalline structure. Conceptually, it is more appropriate to start from an amorphous network, and then perform bond dilution on it, thus creating a sequence of random networks with different mean coordinations. We use a 512-atom covalent random-network model of *amorphous* diamond (Djordjević *et al* 1995) as this more realistic underlying structure (figure 2). Of course it would be better still to build a new random-network structure for each value of $\langle r \rangle$, but this is not possible at present.

Our *amorphous* diamond network is fully fourfold coordinated and has stress stored in both the bond-stretching and bond-bending parts of Keating potential (1). This is an important difference with respect to earlier work where the starting structure was a stress-free crystalline lattice. In the present case, the removal of a certain number of bonds releases a significant amount of elastic energy. Thus, while the internal strain energy is always zero when the crystalline lattice is diluted, here the strain energy drops from the initial value that it has in our amorphous diamond model, to nearly zero near the transition point $\langle r \rangle = 2.4$. In fact, we do not expect the strain energy to become exactly zero at the mean-field critical mean coordination, because at the critical point there are still many isolated rigid regions which do not percolate, but which lock in a certain amount of strain energy. As they are isolated, it will probably happen that they do not have any impact on the macroscopic

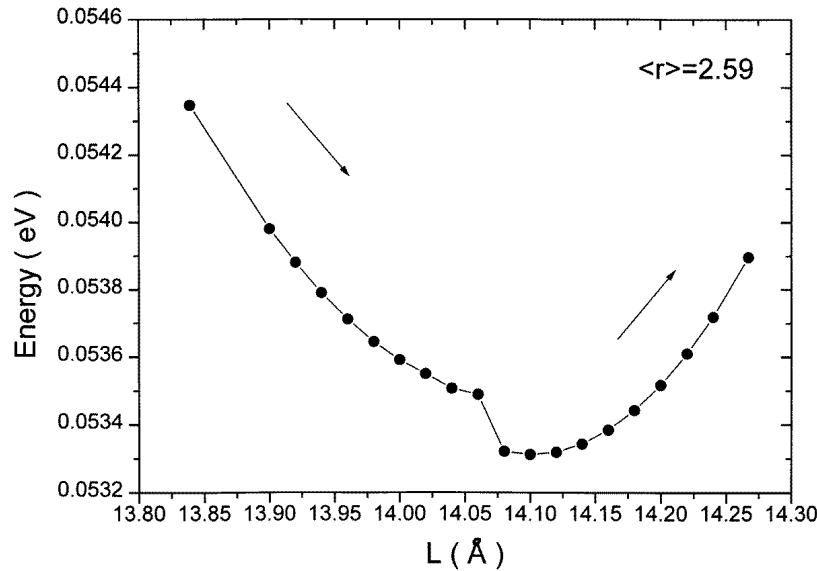


Figure 4. The system is systematically redefined by increasing the size of the supercell (arrows). The energy values all follow a parabolic curve, until a jump to a lower energy state occurs, and the second parabolic curve is created. Energy is in eV per atom, with mean coordination $\langle r \rangle = 2.59$.

stiffness of the structure as described by say the bulk modulus. However, this question remains not fully resolved at this stage of our understanding of the rigidity–percolation phase transition (Jacobs and Thorpe 1995, 1996).

We designed schemes that remove bonds from the amorphous diamond network in several different ways. The obvious one does not impose any restriction except that it forbids the creation of dangling bonds, thus fixing the possible atomic coordination as 2, 3, or 4. As a consequence, when a large number of bonds are removed, such as when $\langle r \rangle \rightarrow 2$, there are many polymeric chains (i.e. 2-coordinated sites) in the structure. Of course, if one wants to decrease the mean coordination all the way to 2, many such long linear chains must form. But if we are mainly interested in the region $2.3 < \langle r \rangle < 4.0$, then we can construct various random networks with the same $\langle r \rangle$. For example, at $\langle r \rangle = 2.59$ we have made *four* different structures. The first has already been mentioned—it has long polymeric chains. The second has only short polymer chains that contain no more than *three* twofold-coordinated atoms. The third has only *two*-atom polymer chains, and in the fourth all the twofold-coordinated atoms are isolated from each other. It was possible to construct random networks with different types of chain for even lower values of $\langle r \rangle$, but we did not explore this in detail. For our calculation of the bulk modulus presented here, we used only the first, non-restrictive style of bond removal, so polymeric chains are present in all of our random structures at low $\langle r \rangle$. This was the same scheme as was used by He and Thorpe (1985) for the depleted diamond lattice.

The initial structure is a fully connected amorphous diamond network with a mean coordination $\langle r \rangle = 4.0$. To avoid any possible correlations between our random networks in a sequence of different $\langle r \rangle$, we adopted the following strategy. First, we remove a small number of bonds, say 20, relax the lattice using the Keating potential, and calculate the mean coordination $\langle r \rangle$, and the total strain energy. We repeat this process 10 times using

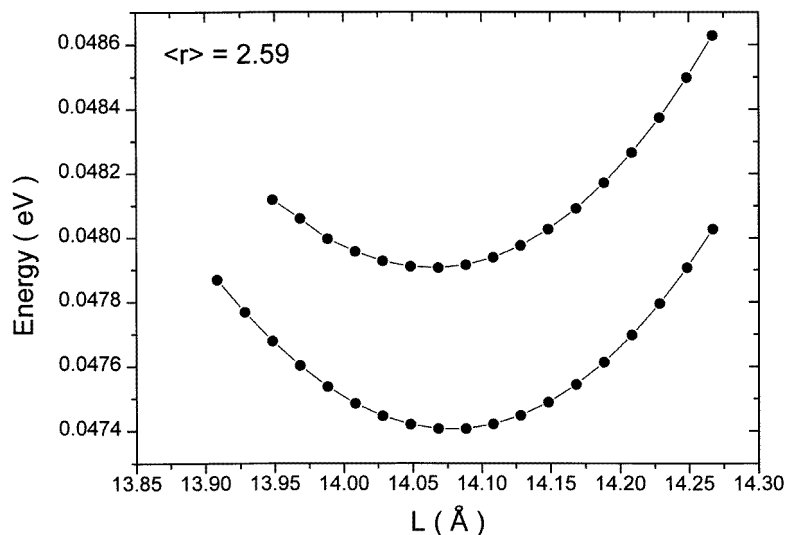


Figure 5. The picture shows two different energy minima which are characteristic for amorphous materials. Energy is in eV per atom, and the mean coordination $\langle r \rangle = 2.59$. This is a different though similar configuration to that shown in figure 4

different random-number generators, and so produce 10 samples for a given $\langle r \rangle$, over which we perform an average. To further decrease the mean coordination, we do not continue from the structure that has been previously obtained, but rather we go back to our fully connected amorphous diamond network, and remove now 40 bonds, relax the diluted system and calculate a new, smaller, value of $\langle r \rangle$ for 10 different samples. In the next step, we go back to the initial structure and remove 20 more bonds (i.e. 60 bonds in total), etc. Each time that we increase the number of removed bonds, stress is released from the initial amorphous diamond structure and the total elastic energy decreases.

It has been already reported (He and Thorpe 1985) that the relaxation process becomes very difficult for approximately $\langle r \rangle < 2.6$, even when the crystalline stress-free lattice is used for bond dilution. In that range of mean coordinations, He and Thorpe used an extrapolation technique to obtain the behaviour at longer times (i.e. a larger number of steps in the relaxation procedure) than could be easily probed. In our calculation, we did not need to use any extrapolation techniques as we ran the relaxation processes for more steps. In figure 3 we show the total strain energy as a function of the mean coordination $\langle r \rangle$.

For large mean coordinations the relaxation is very fast, and only 500 relaxation steps are needed. For small mean coordinations the number of relaxation steps has to be increased considerably to achieve convergence. The required accuracy was kept constant, and the number of relaxation steps was varied so that, at small mean coordinations, more than 50 000 steps were needed.

3. The bulk modulus

Repeating the basic approach presented in the work of He and Thorpe (1985), we calculate the bulk modulus $B \equiv (c_{11} + 2c_{12})/3$ as a function of the mean coordination $\langle r \rangle$. The calculations are more difficult here as the equilibrium structure has to be obtained first by

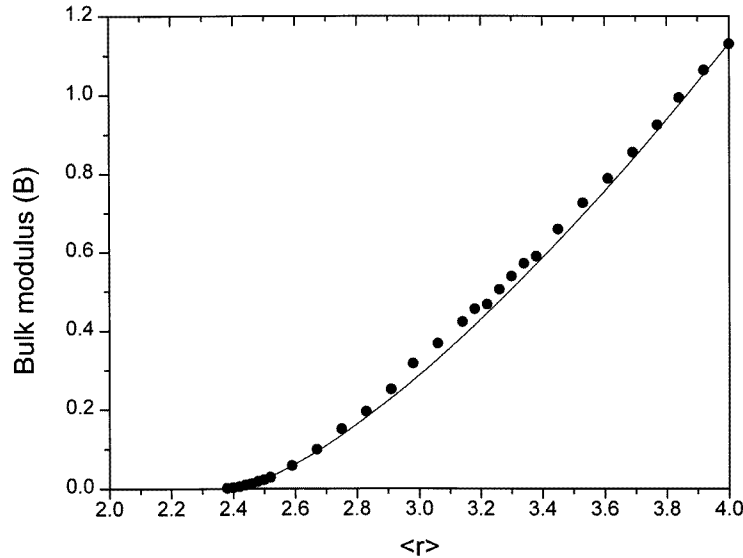


Figure 6. Dots represent our result for the bulk modulus B as a function of the mean coordination $\langle r \rangle$, for a bond-depleted *amorphous* diamond lattice. Each dot is obtained from the curvature of a parabola like one of those in figure 5, and averaged over 10 configurations. The solid line represents the bulk modulus obtained by bond depletion of the *crystalline* diamond lattice (Franzblau and Tersoff 1992). $\gamma_c = 0.655$.

relaxation, *before* the elastic moduli can be found, by further relaxation.

The bulk modulus B was calculated in a standard way by redefining the size of the supercell uniformly along all three coordinate axes. For each mean coordination, we have included the supercell size as a variable in the relaxation subroutine. In this way the structure is relaxed not only with respect to the α - and β -forces in the Keating potential, but simultaneously also with respect to the size of the supercell. Starting from that optimal supercell size, we redefined the supercell four times—two times increasing the supercell size *sequentially*, and two times decreasing the supercell size *sequentially* with respect to the original optimal size which minimizes the total elastic energy. By *sequentially*, we mean that we take coordinates of the atoms when the supercell is of optimal size, and apply a small uniform strain which slightly compresses the lattice. Then we relax the structure with the Keating potential, calculate the new coordinates of all of the atoms, and apply the same strain again, using the updated coordinates from the previous configuration. In this way we obtain the values of the total strain energy at *five* different supercell sizes. These points should, in principle, form a parabola. The bulk modulus B is, up to the constant prefactor, equal to the curvature of that parabola.

An interesting effect that arises when diluting our amorphous underlying structure is that one can spontaneously and unpredictably jump from one *metastable* state to another. If that happens, one has to reject that situation, and to repeat the search for parabolic energy dependence again. This occurs very often and makes the computation very slow, if one does not first find the minimum energy with respect to the supercell size (Mousseau 1996a). This is why we implemented simultaneous minimization of the energy and the supercell size. When that minimum is used to redefine the supercell, it is very rare that the system jumps from one metastable state to another.

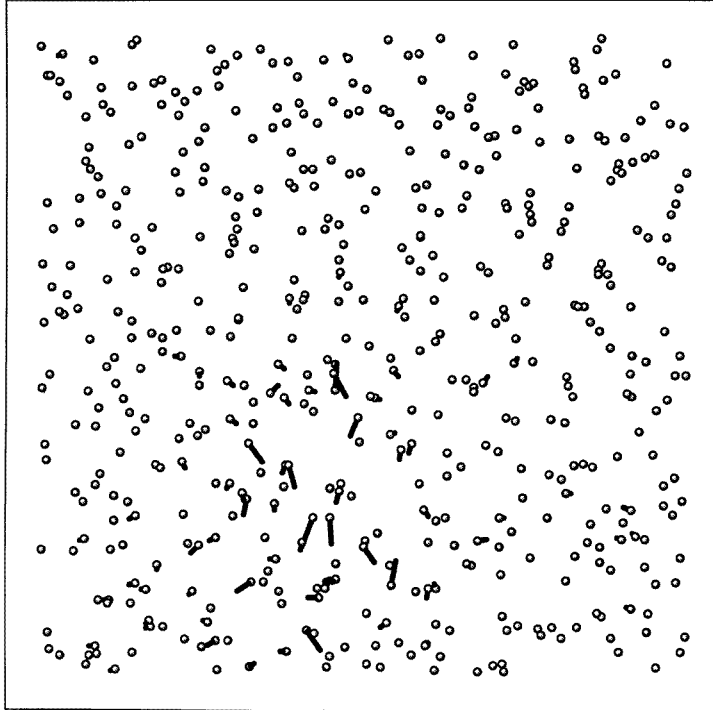


Figure 7. The picture shows 512 atoms in their positions which corresponds to one of the states described by parabolas in figure 5. The black bars represent the displacements of some atoms which give rise to the existence of the second state. The mean coordination is $\langle r \rangle = 2.59$.

In figure 4 we show a typical jump in energy which occurs in these amorphous networks. With careful examination we were able to reconstruct the *missing* parts of the two parabolas, thus obtaining two different minima which correspond to two metastable states of the system, as shown in figure 5.

It should be noted here that, once we find a smooth parabola which describes the total strain energy dependence on the supercell size, we do not know whether that parabola represents the lowest energy state. We compare the bulk moduli calculated from the two different parabolas, and find that to good accuracy we obtain the *same* result for the bulk modulus, regardless of which parabola we use. This is a very interesting observation whose full consequences require further consideration.

In figure 6 we show our computed bulk modulus B as a function of the mean coordination $\langle r \rangle$. It is clear from figure 6 that the underlying initial structure, from which a random network is obtained by bond dilution, does not make any significant difference in the behaviour of the bulk modulus. Our amorphous starting network, upon the bond depletion, produced a bulk modulus which almost exactly follows the power law of Franzblau and Tersoff (1992) as given in equation (3). The small discrepancy for the middle range of mean coordinations could be a consequence of the poor statistics that we had in our calculation because of using only 10 samples for averaging. The other possibility is the fact that Franzblau and Tersoff (1992) do not give the explicit value of the force-constant ratio γ_c apart from stating that this is the diamond value. We have used $\gamma_c = 0.655$ which is the value that we had in our amorphous diamond model (Djordjević *et al* 1995).

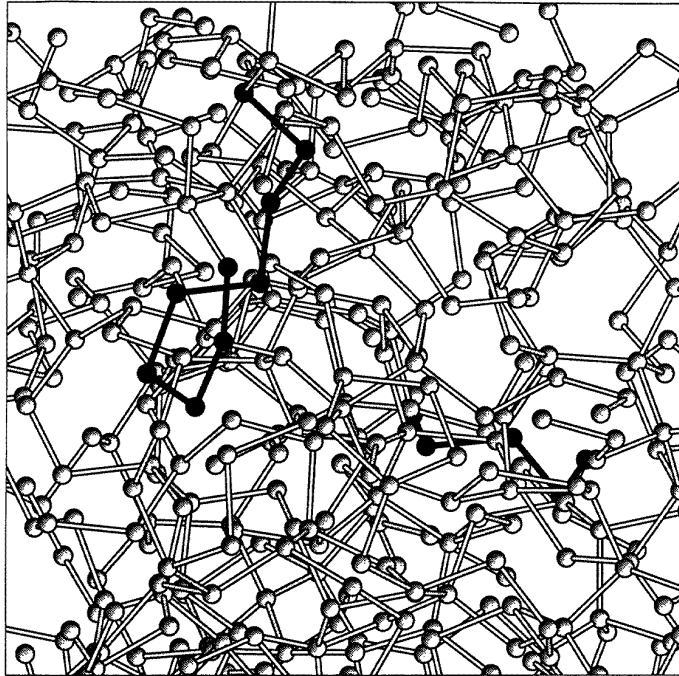


Figure 8. The picture shows polymeric chains of atoms in black that are involved in the motion which gives rise to the existence of two states for a structure with $\langle r \rangle = 2.59$.

4. Metastable states

We have investigated the nature of the two states that appear in our bond-depleted amorphous structure in more detail. It became clear that the value of the energy minimum does not depend only on the supercell size, but also on the particular *history* of changes that were imposed upon the system. We were able to identify the atoms whose motion is responsible for the existence of these two energy states. Comparing the atomic coordinates of the structure in these states we made a picture which shows 512 atoms in one of the states while the black bars that are drawn represent the displacement of the given atom to another position which it has when the structure is in the *other* metastable state. Thus a relatively small fraction of atoms are repositioned which gives rise to the existence of a second metastable state. This is shown in figure 7. Using the neighbour list for the structure, we identified the connectivity of the atoms involved in that motion. It turned out that all atoms that move belong to polymer chains, as shown in figure 8.

We spent some time searching for two states with a particularly small difference in energy, hoping to find so-called *tunnelling modes* that exist in amorphous systems. A common characteristic of most amorphous materials is a quasilinear term in the specific heat at low temperatures. This has been interpreted phenomenologically in terms of a tunnelling model, in which atoms, or groups of atoms, tunnel between the two lowest energy states in a double potential well (Phillips 1972, Anderson *et al* 1972, Phillips 1985). This tunnelling is a very subtle process which involves energy differences of about 10^{-4} eV (Cusack 1987). Detailed microscopic models for the tunnelling process are still lacking. There were attempts to create a tunnelling model which would explain the anomalous properties of vitreous silica

(Vukcević 1972), and an early computer simulation of tunnelling states in random-network glasses for a-Si and a-Ge (Smith 1979). In spite of these and other attempts, a satisfactory microscopic model for tunnelling modes still does not exist. We were not successful in our search for tunnelling states in our random networks. From figure 4 one can see that the typical total energy difference between the two states that we have in our structures is about $512 \times 0.0002 = 0.1$ eV which is a *three orders of magnitude* larger energy than the one typically involved in the tunnelling modes. Nevertheless, detailed analysis of the energy minima in our random networks helped us to develop a scheme which finds the regions of parabolic energy dependence on the applied strain, which was necessary for extracting the value of the bulk modulus B .

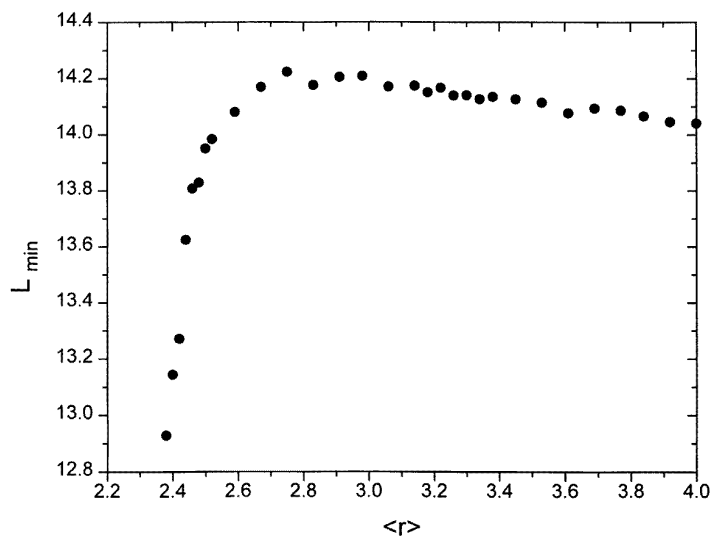


Figure 9. The optimal supercell size which minimizes the total energy, L_{min} , as a function of the mean coordination $\langle r \rangle$. The lengths are given in Å.

An interesting result from our simulations is the behaviour of the optimal supercell size L_{min} , i.e. that one which minimizes the total strain energy at a given $\langle r \rangle$. In figure 9 we show that as more and more bonds are removed from the initial amorphous diamond structure, the optimal supercell size first slightly increases until about $\langle r \rangle = 2.7$ is reached. Further reduction of the mean coordination is followed by a sudden decrease of the optimal supercell size.

We interpret this behaviour as a collapse of the network due to the presence of the long linear polymeric chains. The twofold-coordinated atoms in these chains can come arbitrarily close to each other, because of the lack of an exclusion volume that initially existed due to the tetrahedral coordination of the amorphous network. To test this hypothesis we calculated the pair distribution function for four different mean coordinations, $\langle r \rangle = 2.44, 2.75, 3.06, 3.38$ (figure 10). At small $\langle r \rangle = 2.44$ there are many peaks close to the origin, before the first and second peak that correspond to the nearest-neighbour, and the next-nearest-neighbour distance in the fully connected amorphous diamond, respectively. These additional peaks that occur at very small distances are a consequence of the *collapse* of the network when the twofold-coordinated atoms in adjacent polymer chains come very close together. If we artificially introduced an exclusion volume around each atom in the network, the collapse

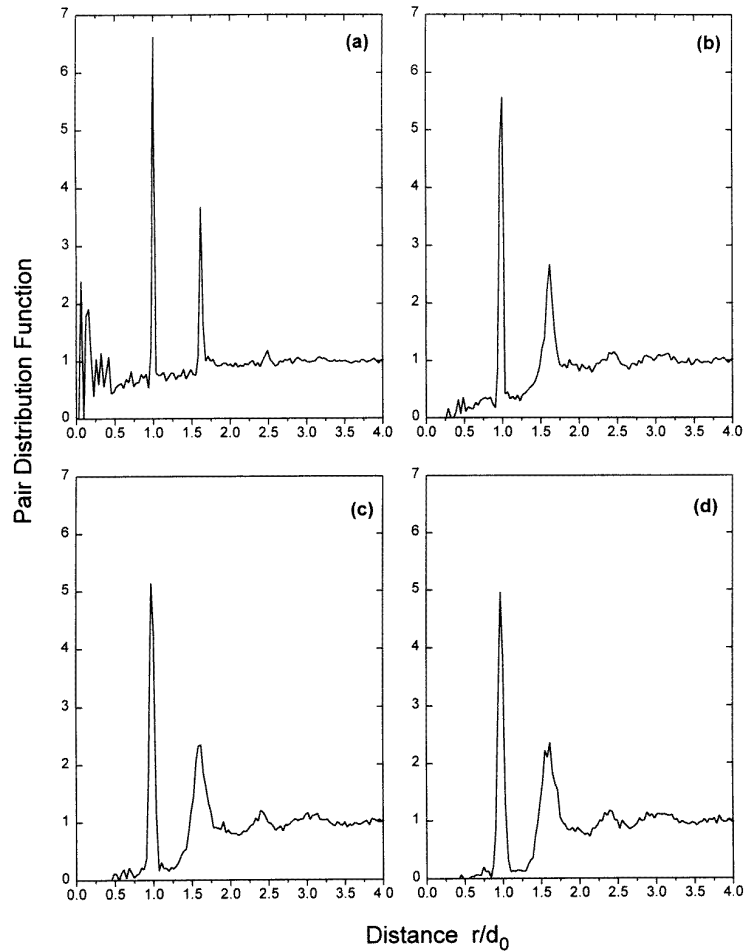


Figure 10. Pair distribution functions calculated for $\langle r \rangle = 2.44$ (a), 2.75 (b), 3.06 (c), 3.38 (d).

would not occur (Mousseau 1996b). Collapse is triggered by the stress that is present in the initial amorphous diamond network. As we said, at small $\langle r \rangle$, a large number of bonds are first randomly removed from the fully connected amorphous diamond network. Because of that, the stress in the network suddenly drops and the atoms are free to move toward the equilibrium positions—which occurs in the process of relaxation. In earlier work of He and Thorpe (1985) and of Franzblau and Tersoff (1992), where the underlying structure for bond removal was a stress-free crystalline diamond lattice, such a triggering mechanism was absent because the equilibrium random network has zero strain energy for all mean coordinations.

5. Conclusions

Earlier calculations of the elastic properties of amorphous networks were done assuming that the bond dilution of a *crystalline* lattice, and the subsequent relaxation, gives an acceptable sequence of amorphous networks, which is suitable for the calculation of the

elastic properties. In our simulations, we have used a true *amorphous* structure for bond dilution, and calculated the bulk modulus as a function of the mean coordination. Our results show that in the two cases the bulk modulus obeys practically the same power law, which suggests that for the elastic properties, the topology of the initial structure (before the bond dilution takes place) is not of any importance. It is the *mean coordination* alone which determines the elastic properties.

We have only presented results for the bulk modulus B in bond-depleted diamond-like networks. However there is little reason to think that other elastic moduli or different values of the force-constant ratio $\gamma = \beta/\alpha$ would lead to any conclusions. It should be noted that the singularity at around $\langle r \rangle = 2.4$, and hence the power-law behaviour, is rounded in reality because of the existence of weak dihedral and other forces (Cai and Thorpe 1989).

We have described the difficulties encountered in dealing with a true amorphous structure which contains large internal strains, which are connected with different energy minima, i.e. different metastable states, that exist in amorphous materials and are associated with polymeric chains of atoms, that can *tunnel* between different local minimum. It should be noted that the tunnelling energy found here of 0.1 eV is comparable with a phonon energy from the Keating potential. It may be that a more extensive search could turn up metastable minima that are much closer in energy (10^{-4} eV) that would be candidates for tunnelling states that are effective at low temperatures as observed in experiments.

Acknowledgments

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