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A STUDY OF THE STATISTICAL MECHANICS OF SILLIUM

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The Sillium Model provides a straightforward method for the simulation of the structure of amorphous silicon or germanium. The Keating potential is used to crudely model the forces associated with tetrahedral bonding and only fourfold coordination is allowed. This enables structures to be randomised and annealed using a simple bond-switching process only. Originally invented merely as an *ad hoc* procedure, this has proved very successful and now seems worthy of closer scrutiny: we present such an analysis in a preliminary form.

KEY WORDS: Sillium Model, silicon, germanium, Keating potential, tetrahedral bonding

INTRODUCTION

We present some recent work on the computer simulation of a continuous random network model of amorphous materials. The Sillium Model describes a network of tetrahedrally bonded atoms interacting through a Keating potential. This model has been defined and described elsewhere [1]; here we give only a brief description. We have been using computer simulations to study the thermodynamic behaviour of the system at different temperatures. An analytical model of topological rearrangements taking place in the network has also been developed, the results of which are compared and contrasted with simulation data.

The Sillium Model

The Sillium Model may be briefly defined by the following set of rules:

- 1) Each atom is bonded to four neighbours
- 2) The total energy of the system is given by the sum of bond-bending and bond-stretching terms, as described by the Keating potential. No vibrational motion is considered.

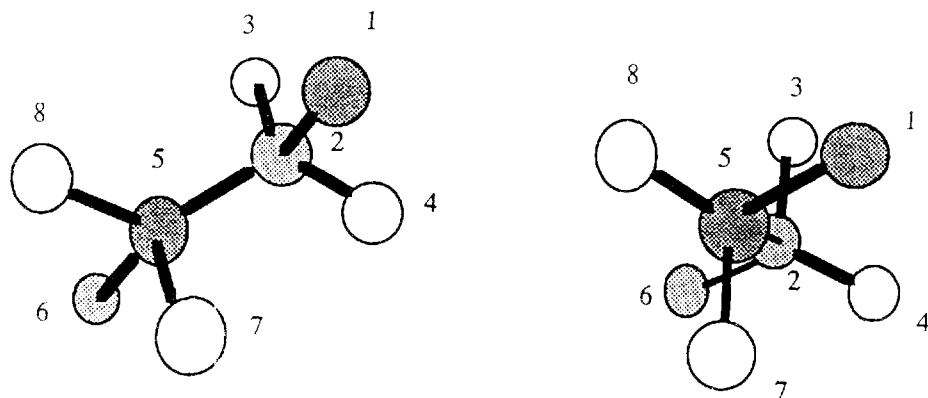


Figure 1 Rearrangement of bonds used to generate random networks; only parallel bonds may be exchanged.

- 3) The only degrees of freedom consist of bond switches or rearrangements, which shall be described in more detail below.
- 4) Periodic boundary conditions are employed for the system of atoms (usually 216 atoms, 432 bonds).
- 5) Monte Carlo rules are used to carry out the structural rearrangements of bonds at different temperatures.

Simple bond rearrangements that do not introduce excessive network distortion are employed. As shown in figure 1, a bond rearrangement exchanges two more-or-less parallel bonds, labelled as (6,5) and (2,1), around the central bond (2,5). A relaxation procedure is then used to bring the network to a geometrical configuration of minimum energy after a switch has been introduced.

Geometric relaxation is accomplished in the following manner. The forces acting on an atom are calculated for each atom in turn, the atom being moved to its approximate position of equilibrium under the bond-stretching and bond-bending force due to its nearest and next nearest neighbours. Each atom is repositioned in turn, the process being repeated over enough cycles so that convergence to equilibrium is reached for the entire structure, with sufficient accuracy for the purposes at hand.

In practice two bonds are switched on a random basis and the energies of the two structures compared. If the new structure has a lower energy, it is accepted; if the energy is higher, it is accepted with probability $\exp(-dE/kT)$, where dE is the energy difference between the two configurations and T the temperature.

One can obtain randomised networks by introducing large numbers of topological rearrangements into the ground state diamond cubic structure. Realistic amorphous networks can be attained by simulated annealing [2], which brings a randomised (and highly distorted) structure down to a low energy amorphous state.

The Independent Bond Model

In order to develop a quantitative theory of the effects of topological arrangements in the network, we must look more closely at the nature of the individual switching

process. First consider the introduction of switches (or so-called "defects") into a crystalline network. Because of the constraint that bonds chosen for switching must be approximately parallel, there are only three possible rearrangements that can be introduced around one bond (between any two neighbouring atoms).

Furthermore, if rearrangements are applied repeatedly between the same two atoms, only a finite number of bonding configurations are produced. Four distinct configurations can be obtained in the case of an isolated defect: the original ground state and three excited states raised by ΔE above the ground state. Thus one may consider the switching process as consisting of excitations of the bond around which the rearrangements take place. In the Sillium network ΔE is approximately equal to 4.5 eV.

In certain cases we expect the introduction of switches to be a spatially independent process. That is, the introduction of a switch at one point in the network should have no effect on the introduction of a switch at another point. This is a reasonable assumption when small amounts of rearrangements have been introduced into a crystalline network.

In reality, however, the introduction of switches is not independent, as a rearrangement changes the network structure over nearest and next-nearest neighbours. In a random network the excitation energies vary over a continuous range of values; in fact, the spectrum of excitation energies broadens with increase in defect concentration, while at the same time the average defect energy decreases [1].

By making the simplification of independent excitations associated with bonds, an analytical model for bond rearrangements can be developed. From the rate equations for a two-level system separated by energy ΔE (one ground state and three excited states) we can find a relationship for N_s , the number of bonds in an excited state, using appropriate initial conditions. The total energy for a N -bond system is then given by the product $N_s \Delta E$, which as a function of temperature and time is found to be

$$\langle E(T, t) \rangle = \frac{3N\Delta E \exp(-\Delta E/kT)}{1 + 3\exp(-\Delta E/kT)} (1 - e^{-Wt}) \quad (1)$$

where W is a transition rate. The equilibrium conditions for this model are found by letting $t \rightarrow \infty$.

By employing a mean field approach the effects of defect interaction can be approximately taken into account. This is done by setting the defect energy to be a function of defect concentration, so that the total energy has to be recalculated in self-consistent manner, for each value of time or temperature.

First let us propose a relationship between ΔE and the number of bonds in the excited state (corresponding to the number of defects present) by reference to the properties of the Sillium network. We expect the excitation energy to be equal to ΔE at small concentrations, ie

$$\Delta E(N_s) = 4.5 \text{ when } N_s = 0.$$

On the other hand for a network that is very disordered, we expect the introduction of a defect to increase or decrease the energy of the system with equal probability so that we may write

$$\Delta E(N_s) = 0 \text{ as } N_s \rightarrow \infty.$$

The exact functional relationship between the above values is not known but we have taken it to be exponential. That is

$$\Delta E(N_s) = C_1 \exp(C_2 N_s).$$

From the above conditions we must have that $C_1 = 4.5 \text{ eV}$ and that C_2 is negative. The absolute value of C_2 may be found by fitting to simulation data.

SIMULATION RESULTS

During the course of work, in an effort to reduce computer running time, we found that significant reductions could be made by allowing greater freedom of topological arrangements. Earlier versions of the program had disallowed the creation of both 3 and 4-fold rings when introducing a switch and had a restrictive method of choosing bonds as possible candidates for switching. In fact, by calculating the energies of all the possible switches admissible between two atoms it was found that the program occasionally disallowed switches that could sometimes be energetically favourable. A method that switched bonds that were the "most parallel" was successfully introduced, cutting computer running time significantly.

To study the process of introducing topological disorder into the crystalline network, we introduced defects into the diamond cubic structure at a fixed temperature. The results shown in figure 2 show such a randomisation procedure at $kT = 2.0 \text{ eV}$ for 215 atoms. From the plot of the increase in energy of the system as a function of time (in Monte Carlo steps) one can see that the network becomes saturated after about 2000 steps, giving a rough measure of the time it takes to reach equilibrium at that temperature from the ground state. The diagram also shows the predictions of the independent bond model, as given by equation (1) with $kT = 2.0$ and N , the total number of bonds, equal to 432. As can be seen from this figure, the independent bond model energy rises more rapidly than that of the sillium network.

Of more interest is the behaviour of the system as a function of temperature. This was studied by raising the temperature linearly with every Monte Carlo step by

$$T = T_0 + \alpha t.$$

choosing the value of α so that T was raised slowly enough for the system to come to quasi-equilibrium at every stage. Results of the heating process are shown in figure 3, which shows the effect of raising the temperature up to $kT = 2.0 \text{ eV}$ over 12000 MC steps. From this graph we can roughly identify a "melting" transition at about $kT = 1.0 \text{ eV}$, which is in agreement with an estimate taken from the sudden change in the structure factor found to occur at this temperature [3]. More MC steps are required to estimate the transition with a reasonable degree of accuracy, as in this region fluctuations are particularly evident. We also note that the energy reached at the end of heating ($kT = 2.0 \text{ eV}$) is approximately 420 eV . This confirms that the system is near equilibrium, since the same energy was reached by randomisation at the fixed temperature of $kT = 2.0 \text{ eV}$; see Figure 2.

Figure 3 also shows the predicted values of energy from the independent bond model and the mean field approximation, both showing reasonable agreement in the range of temperatures simulated, except in the region $kT = 1.0 \text{ eV}$, where fluctua-

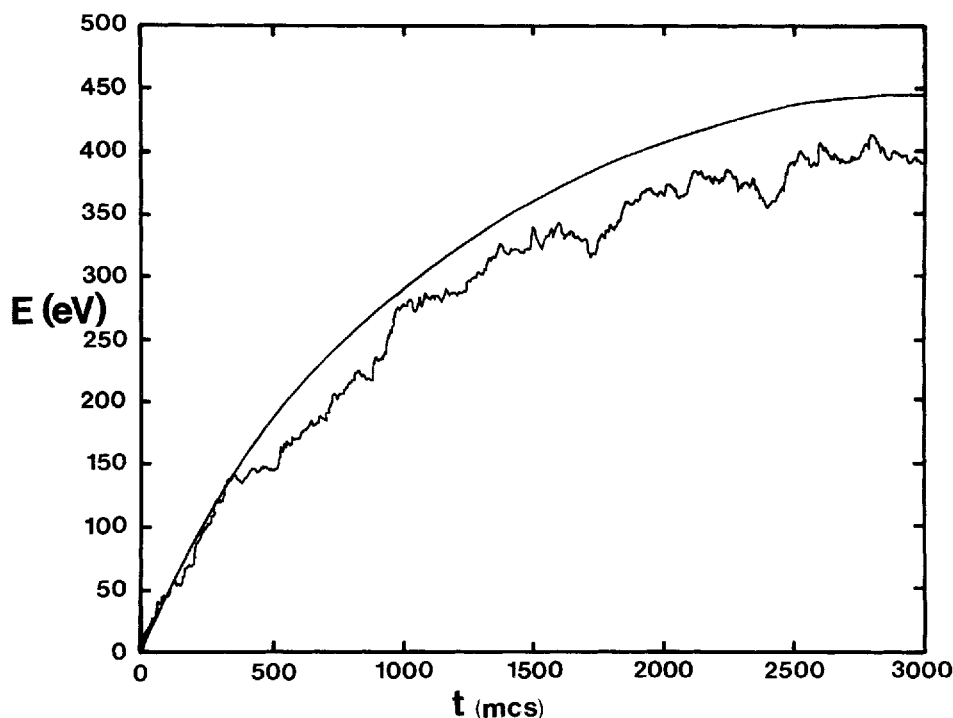


Figure 2 The total energy of the network increases with the introduction of defects. Temperature was fixed at $kT = 2.0$ eV throughout and time is measured in Monte Carlo steps. The smooth curve is the prediction of the independent bond model.

tions are strong. The predictions of the independent bond model were found by taking equilibrium values of equation (1) ($t \rightarrow \infty$), and plotting as a function of temperature. The parameter (C_2) in the mean field correction was chosen so that the value of the energy corresponded to the equilibrium value of the network simulation at $kT = 2.0$ eV. As we have seen in Figure 2 the equilibrium energy is about 420 eV at this temperature.

We have also investigated the minimum energy reached for amorphous structures for different annealing rates, to see whether we could find structures similar to those that had been annealed on a supercomputer [1]. In this case the temperature is decreased exponentially during simulation by

$$T = (\alpha)^t T_0$$

The starting structure used was a network that has been randomised at $kT = 2.0$ eV for 3000 steps, so that T_0 was taken 2.0, and an annealing run was carried out for 10000 steps. Annealing runs almost completely removed 3-fold rings in the network that had been introduced by the randomisation process, confirming that our modified rules still gave the correct type of structure once annealed. Despite the improvements to our algorithms, however, somewhat longer anneal times are still required to obtain structures with a small number of 4-fold rings and with less distortion. As can be seen from Figure 3, the annealing schedule was not able to reduce the energy of the

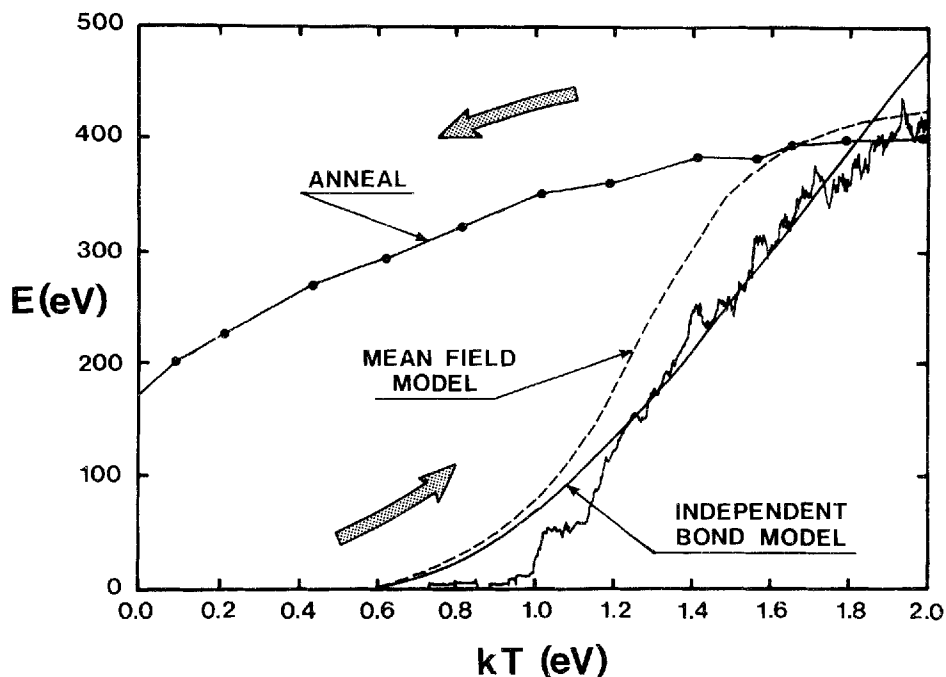


Figure 3 Energy as a function of temperature. The jagged curve is computed for linearly rising temperature, as described in the text. Also shown are (equilibrium) predictions by the independent bond model, mean field correction and results of subsequent cooling by an annealing schedule. The rate used for the anneal as shown in the diagram was $\alpha = 0.9994$

network below 150 eV. Previous calculations succeeded in reducing this energy to 80 eV [1].

CONCLUSION

We realise that our results contain significant levels of noise, and that further simulations still have to be carried out. However, the overall results support the validity of the independent bond model and have given us confidence in using such an approach for further analysis.

Acknowledgement

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APPENDIX: METHODOLOGY

The algorithm used to generate and anneal random networks consists of an iterative sequence of topological rearrangement and geometrical relaxation.

Topological Rearrangement

When carrying out topological rearrangements, two bonds are switched on a random basis and the energies of the two structures are compared. The Metropolis rule is then used to decide whether a switch can be made. If the new structure has a lower energy, it is accepted; if the energy is higher, it is accepted with probability $\exp(-\Delta E/kT)$, where ΔE is the energy difference between the two configurations and T the temperature. Every trial structure produced has to be relaxed and then compared, so that the computational time involved in every Monte Carlo decision is quite lengthy.

Geometrical Relaxation

The potential function used to carry out geometrical relaxation of the structure is the Keating potential, which is given by two terms

$$V = \frac{3\alpha}{16d^2} \sum_{li} (\mathbf{r}_{li} \cdot \mathbf{r}_{li} - d^2)^2 + \frac{3\beta}{8d^2} \sum_{l(i,j)} \left(\mathbf{r}_{li} \cdot \mathbf{r}_{lj} + \frac{d^2}{3} \right)^2$$

Here α and β are the bond-stretching and bond-bending force constants, and d is the equilibrium Si-Si bond length in the diamond structure. The first term gives the sum of the bond stretching for the whole network by summing over all atoms l and their four neighbours given by i . The second term gives bond bending contributions by summing over all atoms and pairs of distinct neighbours.

Relaxation is accomplished in the following manner. The forces acting on an atom are calculated for each atom in turn, the atom being moved to its approximate position of equilibrium under the bond-stretching and bond-bending forces due to its nearest and next nearest neighbours. Each atom is repositioned in turn, and the process is repeated over enough cycles so that convergence to equilibrium is reached for the entire structure. In practice, the number of cycles used in order to obtain convergence may be between 10 and 30. At the end of relaxation all atoms are required to be within ϵ of the exact equilibrium values, where ϵ is typically 0.1% of the nearest neighbour distance d .

Overall Iterative Sequence

The iterative sequence of topological switching and relaxation is shown in the diagram. In the computer code, the coordinates of each atom and its nearest neighbours are kept in two arrays. At the first step, corresponding to a Monte Carlo switch, the nearest neighbour table is changed. At the second stage the relaxation takes place and the coordinates of the atoms are changed. A full simulation consists in repeating this sequence many times.