

Simulation of Tunneling States in Random-Network Glasses

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(Received 30 August 1978)

Fully automatic computer simulation of random-network structures in amorphous Si and Ge has been achieved using a generalization of Keating's potential. The local potential for one-atom displacements shows many multiple minima with broad distributions of the energy difference and tunneling matrix element. These distributions lead to reasonable estimates for the specific heat, which behaves as $T \ln T$. One-atom tunneling states appear to be appropriate for amorphous Si/Ge.

The nature of tunneling states in the widely accepted tunneling model of Anderson, Halperin, and Varma¹ and Phillips² for amorphous solids is still unclear, despite the accumulation of experimental findings in its favor.³ However, it is clear from specific heat measurements that tunneling states are a universal feature of amorphous solids or glasses. In a computer search for tunneling states, the simplest solid to model is probably amorphous Si/Ge rather than the glass systems studied so far, since it is monatomic and the coordination (fourfold) is fixed. That the structure is a random network is not in doubt.⁴ Glass formers tend to be covalent bonded with open structures in the glassy and crystalline phases, and so for amorphous Si/Ge we regard covalent bonding as the essential property leading to amorphicity and tunneling states.

To date the best models of glassy random networks have been ball-and-spring constructions subsequently relaxed by computer^{5,6} using Keating's essentially quadratic potential.⁷ These physical models can be eliminated by working with an interatomic potential for covalent bonds. I used a large-amplitude generalization of Keating's potential,

$$V = \frac{1}{2}A \sum_{ij}' f(r_{ij}) + \frac{1}{2}B \sum_{ijk}' g(r_{ij})g(r_{ik})(\hat{r}_{ij} \cdot \hat{r}_{ik} + \frac{1}{3})^2, \quad (1)$$

where primes delete equal indices from the sums. The essential features are a hard core and attractive tail in $f(r)$, and a triplet term which is minimized when two bonds from one atom are at the tetrahedral angle. Taking as unit length the equilibrium bond length d_0 (2.35 Å for Si and 2.44 for Ge), $f(r)$ has minimum value -1 at $r=1$ and $g(1)=1$. Otherwise, the functions were chosen for ease of computation, viz., $f(r) = 15(0.4r^{-6} - 1)(1 - 2r/3)^2$ and $g(r) = 9(1 - 2r/3)^2$ with smooth cutoffs at $r_c = 1.5$. A larger cutoff is desirable but not practical as computing time goes as r_c^6 . The ra-

tio B/A was 1.5, which for potential (1) corresponds to $\beta/\alpha = 0.26$ in the Keating potential.^{5,6} More realistic potentials are not available, but (1) is adequate for our semiquantitative purposes.

To demonstrate that (1) leads directly to acceptable random-network structures, V was minimized for a sample of 250 atoms by the $T=0$ version of a standard Monte Carlo algorithm. The atoms lie within a cube of the appropriate density (0.65) and periodic boundary conditions across cube faces only eliminate most surface effects. Computing time for one Monte Carlo step (MCS) per atom is large because of the triplet term; it is essential to tabulate first and second neighbors of the atom moved, and with $r_c = 1.5$ there are 75 entries on average. The initial configuration of atoms was entirely random.

The results are as follows. After 65 MCS/atom, the distributions of radial separation and bond angles (Fig. 1) have converged to the accuracy of the simulation, and agree broadly with those of Steinhart, Allen, and Weaire⁵ and Duffy, Boudreaux, and Polk.⁶ But there are minor differences. My structures are less "perfect" than the relaxed ball-and-spring models; e.g., in the radial distribution there is no clear separation into first and second neighbor shells, and the bond-angle distribution, while of the same half-width, has a larger standard deviation (19°). It seems plausible that these differences are due to restrictions on bond distortions built into the ball-and-spring models (e.g., no bond lengths greater than 1.3 were allowed). Note that the topology of these models is controlled by arbitrary, and somewhat subjective, rules of thumb used in adding atoms to the structure, and is not changed by subsequent relaxation. Here the concept of bond is not defined *a priori*, and the topology is determined by the energy-minimizing procedure. Counting squares in Fig. 1 shows that fourfold coordination of "bonds" is achieved if the maximum bond length is 1.29, in remarkable agreement with the model-builder's rules. Ring counts

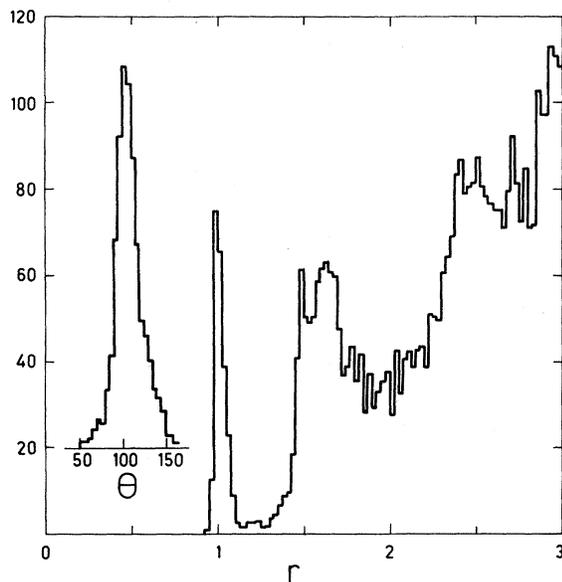


FIG. 1. Radial distribution function and (inset) bond-angle distribution for the relaxed 250-atom model.

were also made, but these appeared to be influenced by boundary conditions and were not characteristic of a bulk structure.

The Monte Carlo method gives each atom in turn a small random displacement which is allowed if the energy drops, whether or not a barrier separates initial and final states. Barriers certainly exist here; so the simulation will not converge to a single metastable state. Convergence of the total energy is slower than for Heisenberg spin-glass simulations⁶; the final energy in units of one bond ($A=1$) was $E = -389$ with a variation of -0.2 per MCS/atom. This incomplete convergence in energy is tentatively interpreted as a slow switching between metastable states, since all atoms are substantially at the minima of their local potentials and all calculated distributions have converged. The rate of switching would be reduced by decreasing the maximum step length of each Monte Carlo move. The presence of a continuous distribution of one-atom energy barriers suggests that the switching rate cannot be reduced to zero for any finite maximum step length. Practically, very small values are undesirable since there is an optimum maximum step length which maximizes the chance of an allowed move. This optimum value decreases as the simulation proceeds and was of the order of 0.01 at the finish. If this switching hypothesis is correct, the energies of metastable states are

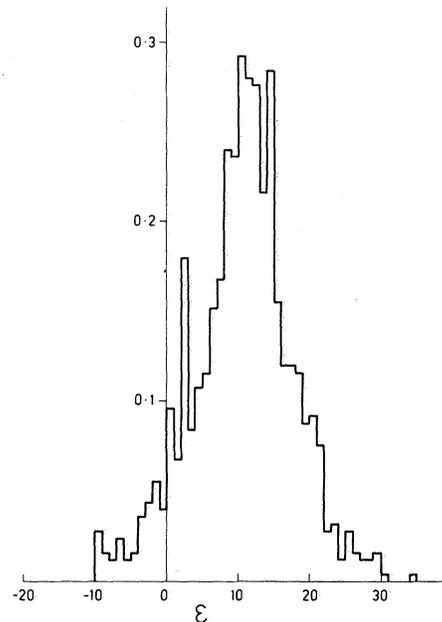


FIG. 2. Density of two-level states per atom, in units where $A=1$. ϵ is positive if the secondary minimum is higher than the original.

likely to be spread widely, although the existence of a heat of devitrification would prevent them from extending down to the crystalline value $E = -500$ for the diamond structure.

A search for one-atom tunneling states was then made by exploring the local potential surface of each atom in turn, the rest of the solid being held fixed. This was carried out by a steepest-descent search from all (100) and (111) directions on a sphere of radius 1.0 centered on the initial equilibrium position. This procedure located 4.05 additional energy minima per atom. The density per atom of the energy difference between new and initial minima is shown in Fig. 2. It peaks at very high ϵ values, viz., about 10 bond energies (10 eV for Si). Most of these states are globally unstable since the cohesive energy is 1.98 units per atom. In fact this distribution is not realized by tunneling atoms since the surrounding structure relaxes during tunneling. A systematic computer study is out of the question, but only low- ϵ states are accessible by phonon-assisted tunneling and these are hardly affected by relaxation if the initial state is well bound. This was checked by moving one such atom to a new minimum with $\epsilon = -0.57$, λ/C [vide (3)] = 0.02 and relaxing the structure for 7 MCS/atom with a maximum step length of 0.005 . Near-

ly all barriers remained intact, with ϵ values changing typically by 5%. However, the same treatment for an atom moved over a large barrier with $\epsilon = 14$ produced a completely different set of barriers. These results contrast with a calculation of Klein *et al.*⁹ who assume all two-level systems are equally affected by strain relaxation.

Tunneling to states with higher ϵ values is the key which "unlocks" the structure. The normal evolution of the 250-atom system with step length 0.005, which is small enough to avoid jumping through barriers, preserved nearly all barriers over 7 MCS/atom. At higher temperatures, tunneling is presumably replaced by thermally activated processes, which may give rise to softening in glasses.

The identification of tunneling states is strengthened by showing that there are enough of them to give the correct order of magnitude for the tunneling specific heat C_t . The standard Anderson-Halperin-Varma-Phillips results are^{1,2}

$$C_t = \frac{1}{6} \pi^2 N k_B^2 T N(0) P(0) \lambda_{\max}, \quad (2)$$

where $N(\epsilon)$ is the one-sided density per atom of two-level states in the energy difference ϵ , $P(\lambda)$ is the distribution of the extinction coefficient λ in the tail of the wave function, and $\lambda_{\max} = \frac{1}{2} \ln \Gamma t$ where $\Gamma \exp(-2\lambda)$ is the transition rate between wells. At 1°K, Γ is estimated as 5×10^{10} Hz for Si and 2.4×10^{10} for Ge from a formula given by Black.³ Thus for a measurement time $t = 10$ sec,

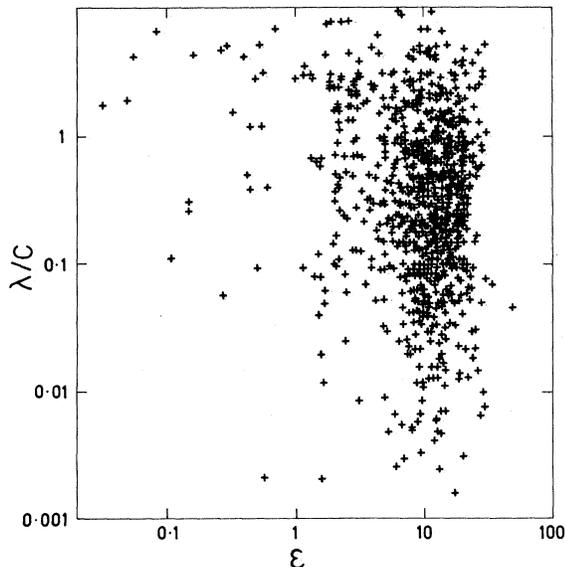


FIG. 3. Scatter diagram of ϵ and λ/C values for two-level states.

$\lambda_{\max} \approx 13$ for Si and Ge. It has been assumed that ϵ and λ are uncorrelated, as suggested by Fig. 3.

The simulation on 250 atoms is too small to reveal any states which would contribute to the specific heat, i.e., with $|\epsilon| < k_B T$ and tunneling times less than t (or $\lambda < \lambda_{\max}$). Hence our distributions (Figs. 2 and 4) must be extrapolated back to zero arguments. There is no reason why they should not be continuous on a finer scale, since bond lengths and bond angles are continuously distributed. λ values were calculated with the WKB approximation, which gives

$$\lambda = C \int_{(\text{minima})} [V(r) - E]^{1/2} dl, \\ C = (2MA/\hbar^2)^{1/2} d_0. \quad (3)$$

I estimate $C = 280$ for Si and 430 for Ge. Figure 4 then verifies that $P(\lambda)$ is flat out to λ_{\max} , which was assumed in (2). Note that the fraction of atoms which tunnel within 10 sec is $\lambda_{\max} P(0) = 0.09$ (Si), 0.05 (Ge).

Table I summarizes these estimates for amorphous Si and Ge. Values of A were derived from crystalline sound velocities by fitting the curvature of the pair potential; larger values are obtained if A is identified as a bond energy but this could be rectified by choosing a more realistic potential. Unfortunately, the specific heats have not yet been measured, but these numbers are comparable with values $C_t/T \sim 10$ ergs/gK² reported for fused silica and glasses.¹⁰

Finally, it should be pointed out that the linear specific heat law is not an exact consequence of the tunneling model. Despite a claim to the con-

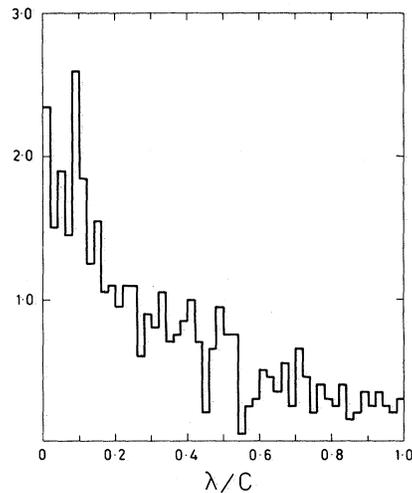


FIG. 4. Normalized distribution of reduced tunneling factor λ/C .

TABLE I. Specific heat estimates.

	A (eV)	$N(0)$ (eV ⁻¹)	$P(0)$	C_t/T (ergs/g K ²)
Si	0.97	0.15	0.007	5.8 (3.5) ^a
Ge	0.83	0.18	0.006	1.6 (0.9) ^a

^aRevised estimates [see discussions in text concerning Eqs. (4)–(6)].

trary,³ it is modified when one considers phonon transitions between eigenstates of the tunneling Hamiltonian rather than between states localized in each well. ϵ is then replaced by $E = (\epsilon^2 + \Delta^2)^{1/2}$ which is the difference between the two energy levels; here $\Delta = \hbar\omega_0 \exp(-\lambda)$ with $\omega_0 \sim 10^{13}$ Hz. The internal energy of these thermalized states is

$$U_t = N \int_0^\infty N(\epsilon) d\epsilon \int_0^{\lambda_{\max}} P(\lambda) d\lambda \frac{E}{e^{\beta E} + 1}. \quad (4)$$

On changing variables from (ϵ, λ) to (E, Δ) and noting that the Δ integration runs from $\Delta_{\min} = \hbar\omega_0 \exp(-\lambda_{\max})$ to $\min(E, \hbar\omega_0)$, (4) in the low-temperature limit $k_B T \ll \hbar\omega_0$ becomes

$$U_t = N k_B^2 T^2 N(0) P(0) I \left(\frac{\Delta_{\min}}{k_B T} \right), \quad \Delta_{\min} = \frac{\hbar\omega_0}{(\Gamma t)^{1/2}}, \quad (5)$$

where

$$I(a) = \int_a^\infty \frac{x dx}{e^x + 1} \ln \frac{x + (x^2 - a^2)^{1/2}}{a}. \quad (6)$$

This differs from the original result, in which I is replaced by λ_{\max} . For long-time measurements $\Delta_{\min} \ll k_B T$ (e.g., for $t = 0$ sec and $T = 1^\circ\text{K}$, $\Delta_{\min} \sim 10^{-3}$ K for Si). In this limit one finds that the leading term for the specific heat is not linear in T but is of the form $T \ln T$.

Revised estimates for the specific heat coefficient appear in parentheses in the last column of

Table I. It is obvious that this modification does not affect the main conclusion of this paper, that there are sufficient one-atom tunneling states to give order of magnitude agreement with specific heat experiments. However, a more careful treatment of (4) may be the key to the puzzling lack of time dependence in the pulsed specific heat measurements of Goubau and Tait.¹¹ For example, a single value of the phonon coupling constant Γ has been assumed for all two-level systems. At high temperatures this is not critical, but when $\Delta_{\min} \geq k_B T$ the main contribution comes from very large values of Γ and so it is essential to allow a distribution of coupling constants.

The author wishes to thank Dr. James Black of the Brookhaven National Laboratory for a helpful discussion.

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