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Molecular-dynamics investigations of conformational fluctuations and low-energy vibrational excitations in *a*-Si:H

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First-principles molecular-dynamics simulations on models of *a*-Si:H and *a*-Si reveal the existence of a quasicontinuous manifold of nearly degenerate and conformationally distinct metastable minima which are accessible to each other at moderate simulation temperatures in the microcanonical ensemble. Other low-energy excitations were also observed: elastic modes with anomalously low frequencies, which are somewhat local, though they involve a significant fraction of the atoms constituting supercell models. We investigate these phenomena via molecular dynamics and relate them to previous work on glassy solids and on liquids.

In the course of studying *a*-Si:H with molecular-dynamics (MD) simulations, we have observed that the supercells never return to the same metastable (or equilibrium) state when quenched. The differences are always small and the topology does not change but the effects are much greater than the uncertainties in the program. This has led us to an investigation of the so-called ''equilibrium state'' which is really a large manifold of very nearly degenerate metastable states, some of which are mutually thermally accessible. The present work is directly relevant to a large corpus of apparently disparate earlier work. In the introductory paragraphs we remind the reader of this work and attempt to put it in the context of the present paper.

As a relatively simple physical model to motivate our findings, consider as we have[1] small clusters of six atoms of Si. Here there are very few energy minima (we discovered four inequivalent minima for Si_6). If one watches an animation of such a cluster, freely vibrating at a high enough temperature, it is easy to see that the system gets ''stuck'' near a given energy minimum for some length of time (essentially executing rather large oscillations about that local energy minimum), then escapes to a region of configuration space nearer another minimum and large, sloppy oscillations persist for some length of time about that minimum, and so on. Naturally, if a rapid quench is performed from a point in the thermal simulation where the cluster is oscillating about a particular minimum, then it is likely that the result of the quench will be that the system will fall into that particular local minimum. In essence this paper is a detailed application of these concepts to an enormously more complex system with a high-dimensional phase space: *a*-Si:H. A number of important conclusions result.

For the case of the amorphous network there is an enormous number of states (scaling like $N!e^{\alpha N}$, where N is the number of atoms and $\alpha > 0$).[2] We will demonstrate that since virtually no bonds are ideal or unstrained, one can subtly alter the system by straining some of the bonds more and some of the bonds less although many atoms have to be adjusted in order to keep the energy change small. The enormous number of multiple minima on the potential energy surface are thought to be a common property of amorphous materials including glasses and polymers.[3] In this paper we show that at least a subset of them are mutually thermally accessible and we investigate the temperature and time dependence of the accessibility. The energy differences between the different minima can be arbitrarily small and the energy barrier to push the system directly from one minima to another is much greater than the energy barrier that the system evolves over in a much more circuitous path via thermal evolution. The above description is, of course, a part of the lore of ''two-level systems'' (TLS's).[4] The low temperature behavior of noncrystalline materials is known to exhibit interesting and sometimes universal behavior. The most famous example is the linear specific heat of many (particularly defective) amorphous solids for $T \rightarrow 0$ and the related and theoretically ubiquitous ''two level systems.'' The TLS's provide a highly successful phenomenological understanding of the low temperature specific heat, acoustic attenuation, and dielectric measurements of many glassy/amorphous systems. However, detailed atomic descriptions of TLS's have been a rarity. This work identifies such TLS's in theoretical simulations of *a*-Si:H, and a detailed atomic description in this case is possible.

This paper will also report on the related subject of low frequency harmonic modes we have observed in several models of *a*-Si and *a*-Si:H. A key set of concepts relevant to low-energy lattice excitations are embodied in the ''floppy mode'' concept advanced by Phillips[5] and Thorpe.[6] The idea is that underconstrained networks of covalent amorphous semiconductors possess some zero-energy modes. In general these are nontrivial and nonlocal modes involving correlated motions of large numbers of atoms. It is now rather clear that the floppy mode picture is essentially correct. For example, inelastic neutron scattering measurements on compound chalcogenide glasses have shown rigid-floppy transitions, in agreement with the constraint-counting theory when weak dihedral angle forces are included.[7,8] In the usual analysis of floppy modes, one considers global quantities (average constraint number). Naturally, it also seems possible that ''local'' floppy modes might arise from locally defective, effectively

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underconstrained, or strained regions in a globally overconstrained network. As Thorpe has pointed out, one can view the current constraint-counting formulation of floppy modes as being effectively a mean-field theory:[9] this work includes salient local dynamical correlations. In this paper, we will show that something akin to floppy modes occurs in supercells of *a*-Si:H which are clearly overconstrained. We note that from a dynamical point of view, the H-terminated Si lacks the full quaternary connectivity of the network and might be implicated in low-energy "floppy" excitations.

Several years ago, Stillinger and Weber (SW) proposed their "inherent structure" (IS) theory,[2] primarily as a tool to investigate the statistical mechanics of the liquid state. SW noted that a given conformation of a system in thermal equilibrium could be associated with another conformation, a local minimum of the system energy functional. By cleverly exploiting this, the statistical mechanics of the problem could be mapped into an alternative form connected with the energetics and multiplicity of the IS—the minimum energy configurations. SW performed extensive calculations of the IS of various model liquids. We have essentially repeated this approach, but for *a*-Si:H and using first-principles forces.[10] We have performed microcanonical thermal simulations on models of *a*-Si:H at temperatures much below the melting point or recrystallization point and find that quenches performed at different points in the thermal trajectory yield spatially inequivalent but nearly energetically degenerate structures. Naively, one would expect that thermally induced spatial distortions would be insufficient to lead to a distinct conformation. However, the prime message of this paper is that these distortions do indeed lead to distinct confirmations. Of course these distinct metastable conformations are not topologically different (for example, the number of dangling bonds is invariant and the composition of nearest-neighbor pairs is not altered). At present, we do not know whether the effects we report here depend qualitatively on the form of interatomic potential employed.

In effect, we provide atomistic evidence for "conformation fluctuations." One can view these shifts between nearly degenerate energy minima as exceedingly low-energy and topologically complex excitations of the amorphous network. Naturally, we interpret the energy minima as the "two (or multi-) level systems" invoked to explain the anomalies in the low temperature specific heat of amorphous solids. Of course the proper low temperature dynamics of the system must be described quantum mechanically; we show that at room temperature some conformational transitions are easily accessible. An early hint that something like this could occur can be seen in our earlier work,[11] which showed that for room temperature thermal simulations of a relaxed version of the 216-atom *a*-Si model of Wooten, Weaire, and Winer (WWW),[12] there were what we termed "geometrical defect fluctuations:" that is, the number of dangling or floating bonds was time dependent (with the number of floating bonds ranging between 0 and 10 for a 216-atom cell). While we do not see topological variations in our distinct minima, our earlier work implies that the effects of thermal distortions for an amorphous environment is not so trivial as one might naturally expect.

We have extensively studied a model of *a*-Si:H we proposed earlier,[13] and designated SiH61.10 (since it has 61 Si and 10 H atoms). Two of the H atoms are passivating isolated dangling bonds and the other eight were introduced in order to remove highly strained regions from the supercell. These eight are passivating dangling bonds in two groups of clustered H. As a consequence of this procedure, this model has no electronic defects or incorrectly coordinated atoms. On the other hand, from the floppy mode perspective, the Si atoms with H neighbors lack the full connectivity of the network, and may be expected to participate in low-energy excitations. As a test of model dependence and finite size effects, we also briefly studied a 216-atom WWW cell with no H atoms and a 240-atom defect-free cell including hydrogen and found qualitatively similar results on comparable time scales. Some care must be taken to ensure that the supercells are stable with respect to real topological changes and the formation of defects.

To quantify these ideas, we allowed a supercell to evolve at a predetermined average temperature (microcanonical ensemble) for several ps. A time step of 0.2 fs was employed. Periodically, we created a snapshot or replica of the system at that time and then rapidly quenched the replica in order to determine the metastable minimum nearest the thermally disturbed state. We define two autocorrelation functions for the ensemble as

$$\Delta\theta(t_1,t_2)=(\Sigma_i[\theta_i(t_1)-\theta_i(t_2)]^2/N)^{1/2} \tag{1}$$

and

$$\Delta r(t_1,t_2)=(\Sigma_i[r_i(t_1)-r_i(t_2)]^2/N)^{1/2}. \tag{2}$$

In Eq. (1) the index i runs over the nearest-neighbor pairs of atoms where r_i is the distance separating a pair and N is the number of such pairs in the supercell. In Eq. (2) the index i runs over all bond angles defined by triads where θ_i is the bond angle formed by one such triad. In this supercell all Si atoms are clearly fourfold coordinated and all H atoms are clearly onefold coordinated so that there is no ambiguity in the definition of a nearest-neighbor pair or triad. The times t_1 and t_2 refer to the quenched configurations. In a crystalline supercell both $\Delta\theta$ and Δr are zero for all pairs of times. These auto correlation functions provide a good measure of how long it takes the system to alter its individual bond lengths and bond angles. For short time differences both correlation functions will approach zero and for long enough times they will approach a constant plus a fluctuating term due to finite size effects.

First, we look in some detail at a MD run at an average temperature of $T=600$ K. This run is typical of our results for temperatures greater than 100 K. A number of other temperatures were studied and will be described below, but these further runs are not explored in as much detail. It should be noted that the repeated quenches employed in calculating the two-time autocorrelation functions are very computer intensive.

Table I displays the autocorrelation functions $\Delta r(t_1,t_2)$ and $\Delta\theta(t_1,t_2)$ for a number of time intervals that are multiples of 0.2 ps. It turns out that at $T=600$ K this is a long enough time interval so that the results from one entry in the table are not correlated with the results from another entry. Notice the rather extreme changes in $\Delta\theta$ and Δr from one entry in the table to the next. These variations, typically a

TABLE I. Autocorrelation functions $\Delta\theta(t_1,t_2)$ for time pairs t_1 and t_2 measured in picoseconds.

$\Delta\theta(t_1,t_2)$ (deg)

t_1	t_2					
	0	0.2	0.4	0.6	0.8	1.0
0		1.09	1.76	1.13	0.98	1.59
0.2			2.72	0.88	1.99	2.57
0.4				2.76	0.85	0.68
0.6					2.03	2.60
0.8						0.66

100 $\Delta r(t_1,t_2)$ (Å)

t_1	t_2					
	0	0.2	0.4	0.6	0.8	1.0
0		0.38	0.64	0.39	0.36	0.57
0.2			0.87	0.42	0.65	0.83
0.4				0.89	0.34	0.27
0.6					0.66	0.84
0.8						0.26

factor of 2, are of course due to the finite supercell size. It appears that one would have to have a supercell with orders of magnitude more atoms in it in order to obtain uniform values. We see that the rms bond angle changes between equilibrium states from one quench to another are about 1°–2° with corresponding changes up to 0.01 Å in bond lengths. These are small changes but much greater than the numerical noise in the program. The numerical noise is less than 0.0001 Å for lengths, 0.0005° for bond angles, and 0.001 eV for the total energy. We further note that the equilibrium states are virtually identical in their average properties. A typical bond angle average for an equilibrium state is 109.17° with a rms dispersion of 9.02°. From one quench to any other this average changes by at most 0.04° and the dispersion by 0.03°. Typical changes are about one-half of this. Changes in average bond lengths are virtually nonexistent and the maximum change in total energy from one equilibrium state to another is 0.044 eV and again the typical change is about half of that. In temperature units, this is an energy of about 500 K or 7.2 K per atom. Thus these states are exceedingly close to each other on the average. This must be true for our results to be believable, since existing experiments show that the macroscopic properties of a-Si:H do not change on a time scale short of months except, of course, at temperatures where the material becomes unstable or when an external agent (like intense light) is applied to the sample.

We need a finer mesh in time in order to obtain the temporal decay to the correlations. This is shown in Figs. 1(a) and 1(b) where $\Delta\theta(t_1,t_2)$ and $\Delta r(t_1,t_2)$ are plotted for t_1 fixed at 0.4 ps with t_2 varying up to 0.7 ps. From this we can see that correlations in bond lengths and angles decay away on a time scale of about 0.2 ps at this temperature. For time differences greater than 0.2 ps, $\Delta\theta$ and Δr are independent of the time difference except for the fluctuations due to finite size effects. As noted earlier, this time is independent of temperature for temperatures greater than about 100 K. Inspection of Fig. 1 suggests that there is for practical purposes a "continuum" of quenched states derived from different thermally induced distortions. It appears that even for very small but finite times, the autocorrelation function does not go to zero; rather it seems to linearly approach 0 as $t \rightarrow 0$. Consequently, even for very short times, the system does not return exactly to its initial quenched configuration. This suggests that there is a quasicontinuous manifold of "equilibrium states," even in our small supercell models. One might have guessed that there would be a "critical" time at which the system "escaped" to another metastable minimum, but this is evidently *not* the case. Also note that the changes in Δr and $\Delta\theta$ are related in a surprisingly linear fashion. Evidently changes in bond angles necessitate similar changes in bond lengths. The behavior exhibited in Fig. 1 has also been observed at other values of t_1 and another temperature. However, in these cases not as many points were obtained.

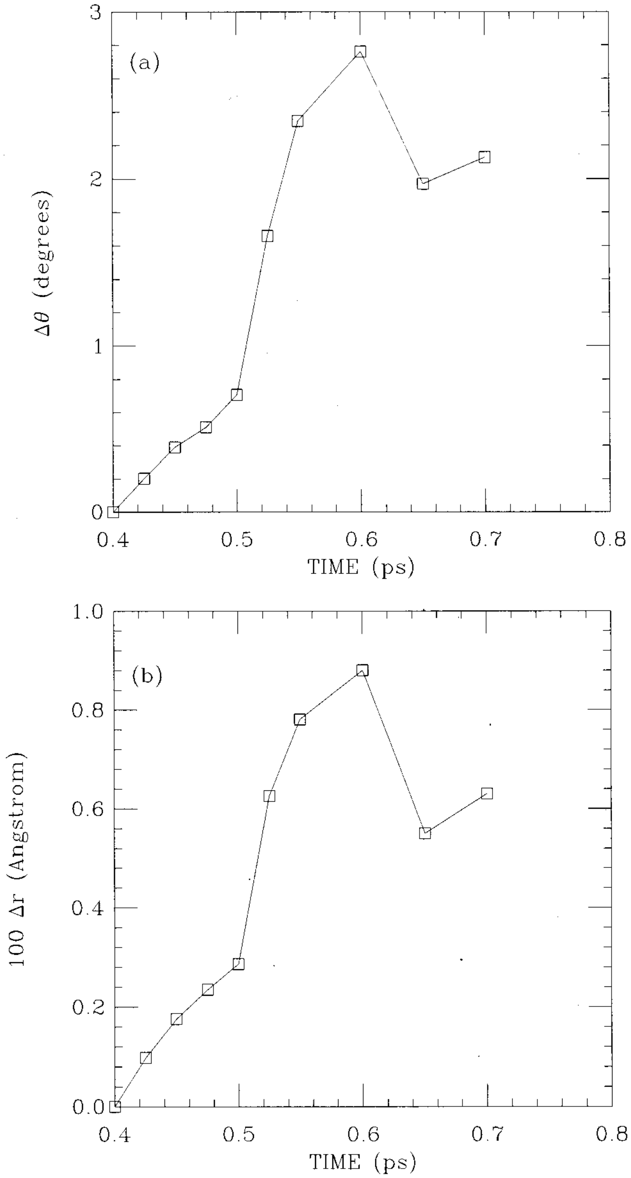

FIG. 1. Autocorrelation function of $\Delta\theta(t_1,t_2)$ and $\Delta r(t_1,t_2)$ for $t_1=0.4$ ps and T_2 varying from 0.4 to 0.7 ps. The temperature is $T=600$ K. Note that the correlations decay away on a time scale of about 0.2 ps. The large fluctuations for times longer than 0.5 ps are due to finite size effects. The lines are merely a guide to the eye.

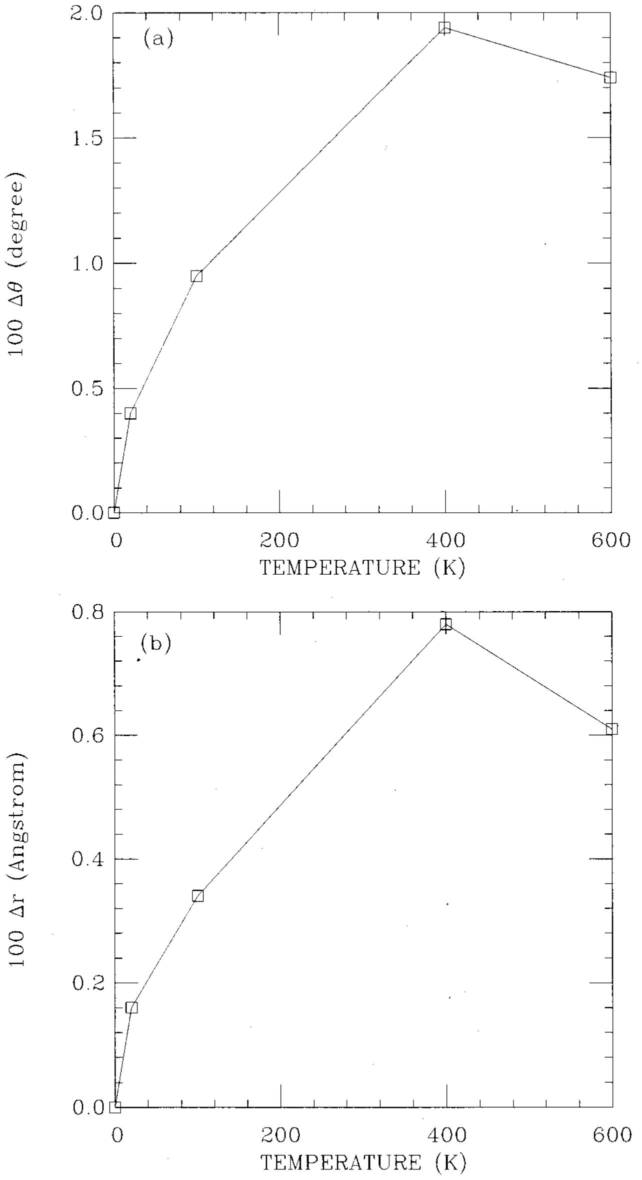

FIG. 2. Average values of $\Delta\theta(t,t+\Delta t)$ and $\Delta r(t,t+\Delta t)$ for $\Delta t=0.2$ ps vs temperature. One can see the characteristic temperature of about 50 K. The lines are merely a guide to the eye.

While changes between the energies of the various equilibrium states are miniscule, the barriers between these states are more substantial. The barrier heights in going linearly from one equilibrium state to another vary between 0.16 eV and 0.19 eV. This is much greater than variation in the equilibrium state energies. However, in a microcanonical thermal simulation the system takes a much more convoluted and lower barrier energy path in going between equilibrium states. This is shown in Figs. 2(a) and 2(b) where the temperature dependence of the effect is shown. At each temperature we have taken an average Δr and $\Delta\theta$ for a number of pairs of quenches differing by times of 0.2 ps. At temperatures above a few hundred degrees, $\Delta\theta$ and Δr are independent of temperature except for the fluctuations due to finite size effects. From the figure one can estimate a characteristic temperature of roughly 50 K. That is, the rearrangement slows down appreciably at temperatures lower than 50 K. At temperatures greater than a few hundred degrees, the autocorrelation functions are virtually indistinguishable. Thus the characteristic temperature is only one-tenth of the direct energy barrier.

Next we briefly discuss the number of atoms involved in the rearrangement process and the dynamics of the process itself. In short, the paths of the atoms in phase space are very complicated and defy any simple description. Between two times that are substantially different, it is rare that any bond angles change by greater than 10°. However, perhaps 30 bond angles change by several degrees. This is about 10% of the total number of bond angles, which is 366. A given H atom is considerably more likely to change its bond angle than a Si atom. However, the bond angle distribution is still dominated by the much more numerous Si atoms. Further, in comparing pairs of equilibrium states, about 50% of the specific bond angles that change by several degrees are the same but 50% are different.

To verify that finite size effects were not important, a limited number of quenches were performed on a defect-free supercell of 240 Si and H atoms as well as a 216-atom WWW supercell. Since we performed much fewer runs, the noise was much greater in this case. However, the results on the larger sample were consistent with our results on the 71-atom sample.

As an additional means of characterizing the low-lying excitations of the system, we have computed the vibrational spectrum and vibrational eigenvectors, both in the 71-atom *a*-Si:H model and in a relaxed version of the 216-atom WWW model. Details of the procedure can be found in Ref. 14. We find low frequency modes (with an energy near 50 cm^{-1}) that are quite complex; the conjugate eigenvectors are somewhat extended, though there is significant additional weight on certain defects in the network. In a crystal, modes

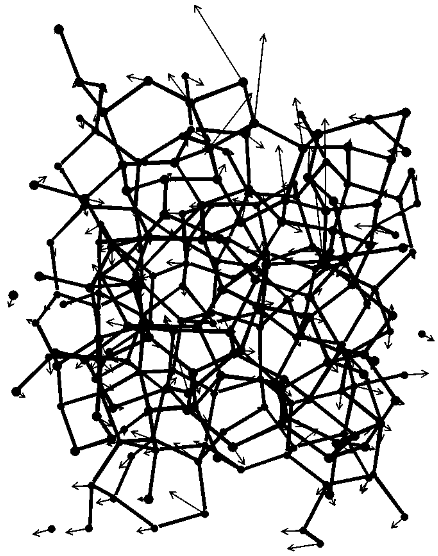

FIG. 3. Lowest energy harmonic mode for relaxed 216-atom WWW supercell. Arrows decorating the atomic positions are normal mode eigenvectors. The mode is most localized on the fourfold ring near the top of the figure. This mode has a frequency of about 56 cm^{-1}, significantly lower than acoustic modes in a crystalline supercell of the same dimensions. Atoms which appear to be undercoordinated are artifacts of the periodic boundary conditions.

at this frequency would be simple acoustic modes. A true ''floppy'' mode would have zero frequency. Since the interactions are of moderately long range and involve many-body interactions it is unrealistic to expect true zero frequency modes. We note that the observed energies of these anomalous modes (a few meV, or thermal energies) are significantly smaller when compared to the lowest frequency crystalline phonon modes in a supercell of the same volume. The modes in question are not well localized, though there is noticeably more weight on atoms in the vicinity of defects. It seems possible that the modes are local, although a proof of this would require a supercell that is much larger than the ones which we used. Earlier work suggests that localization increases with increasing cell size, since then modes cannot interact with themselves. The modes we find are much more complex than the collective tetrahedral modes suggested for *a*-Ge.[17] In Fig. 3 we illustrate this by decorating the atomic positions of the WWW cell with the vibrational eigenvectors for the lowest frequency (nontrivial) mode. The four largest components of the eigenvector are on four elements comprising a fourfold ring, and all the atoms exhibit strong bond angle distortions. In earler work, both Biswas *et al.*[15] and we[16] have noted that both strain and topological defects are very active at the highest frequencies. Here we show that defects are also manifested at the lowest frequencies.

In conclusion, we have demonstrated the existence of a very large number of virtually degenerate energy minima in computer-simulated *a*-Si:H and have partially analyzed the energetics of transitions between these minima. These minima appear to be the states associated with two-level systems. Further, we have demonstrated the existence of very low frequency nonacoustic modes that are very similar to floppy modes discussed in the literature.

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[1] S. Klemm, D. A. Drabold, and O. F. Sankey, in *Atomic Scale Calculations of Structure in Materials*, edited by M. S. Daw and M. A. Schlüter, MRS Symposia Proceedings No. 193 (Materials Research Society, Pittsburgh, 1990), pp. 307; *ibid.*, p. 177.

[2] F. H. Stillinger, Science **267**, 1935 (1995), and references therein.

[3] D. Thorn Leeson and D. A. Wiersma, Phys. Rev. Lett. **74**, 2138 (1995).

[4] A good account of two-level systems and their implications to low temperature properties can be found in *Amorphous Solids, Low Temperature Properties*, edited by W. A. Phillips (Springer, Berlin, 1981).

[5] J. C. Phillips, J. Non-Cryst. Solids **43**, 37 (1981).

[6] M. F. Thorpe, J. Non-Cryst. Solids **57**, 355 (1983).

[7] H. He and M. F. Thorpe, Phys. Rev. Lett. **54**, 2107 (1985).

[8] W. A. Kamitakahara, R. L. Cappelletti, P. Boolchand, B. Halfpap, F. Gompf, D. A. Neumann, and H. Mutka, Phys. Rev. B **44**, 94 (1991).

[9] M. F. Thorpe (private communication).

[10] O. F. Sankey and D. J. Niklewski, Phys. Rev. B **40**, 3979 (1989); O. F. Sankey, D. A. Drabold, and G. B. Adams, Bull. Am. Phys. Soc. **36**, 924 (1991).

[11] D. A. Drabold, P. A. Fedders, S. Klemm, and O. F. Sankey, Phys. Rev. Lett. **67**, 2179 (1991).

[12] F. Wooten and D. Weaire, in *Solid State Physics*, edited by H. Ehrenreich and D. Turnbull (Academic, New York, 1984), Vol. 40, p. 2.

[13] P. A. Fedders and D. A. Drabold, Phys. Rev. B **47**, 13 277 (1993).

[14] D. R. Alfonso, D. A. Drabold, and S. E. Ulloa, Phys. Rev. B **51**, 1989 (1995).

[15] R. Biswas, M. Bouchard, W. A. Kamitakahara, G. S. Grest, and C. M. Soukoulis, Phys. Rev. Lett. **60**, 2280 (1988).

[16] P. A. Fedders, D. A. Drabold, and Stefan Klemm, Phys. Rev. B **45**, 4048 (1992).

[17] U. Bucheneau, M. Prager, W. A. Kamitakahara, H. R. Shanks, and N. Nücker, Europhys. Lett. **6**, 695 (1988).