Reply to "Comment on 'Boson peak in amorphous silicon: A numerical study'"

Frank Finkemeier and Wolfgang von Niessen
Institut für Physikalische und Theoretische Chemie, Technische Universität Braunschweig, Hans Sommer Strasse 10, D-38106 Braunschweig, Germany

(Received 14 February 2002; published 5 August 2002)

Nakhmanson, Drabold, and Mousseau [Phys. Rev. B **66**, 087201 (2002)], preceding paper criticized the model of the present authors [F. Finkemeier and W. von Niessen, Phys. Rev. B **63**, 235204 (2001)] which was used for an explanation of the Boson peak in *a*-Si. NDM criticized the generation of the model and the potential used by us. The low-frequency vibrational density of states $g(\omega)$ of *a*-Si are reinvestigated with the help of an improved structural model using the modified Stillinger-Weber potential. The previously described deviation from the Debye ω^2 behavior is shown to be an artifact caused by an unrealistic high defect concentration. Nevertheless the improved model, which possesses a strongly decreased number of defects, still shows the existence of additional low-frequency modes compared to the crystal, which could be part of an explanation of the boson peak arising already in the harmonic approximation.

DOI: 10.1103/PhysRevB.66.087202 PACS number(s): 61.43.Bn, 63.50.+x, 61.43.Dq

In the preceding comment on our recently published paper,[1] which deals with the origin of the boson peak in *a*-Si, Nakhmanson, Drabold, and Mousseau[2] (NDM) criticize that the properties of our model differ in some important points from experimental findings. Thus it would not be possible to draw any conclusions from our calculations about the nature of low-frequency vibrations in real samples of *a*-Si. The criticism of our original model consists of four main objections: (i) the model is an electronic conductor, (ii) traces of crystallinity are still present in the structures, (iii) the width of the bond-angle distribution is too large, and (iv) the number of coordination defects are too large. Here the points (iii) and (iv) are strongly connected, since an overcoordination or undercoordination results in a deviation from tetrahedron geometry and thus in a broadening of the bond-angle distribution. The reason for the defects of our model is according to NDM an improper implementation of the bond-switching algorithm of Wooten, Winer, and Weaire[3,4] (WWW) and the use of the original Stillinger-Weber (SW) potential.[5]

In this reply, we present some calculations to show that the primary message of our paper holds: already in the harmonic approximation and with a reasonable model of *a*-Si extra low-frequency vibrations, compared to the crystal, appear. We are aware of the deficencies of our models as they are pointed out by NDM. In particular, we agree with points (iii) and (iv), but we want to give the reason for adopting our model and we wish to comment on the other considerations below.

We want to clarify at the outset that our implementation of the algorithms for constructing the models was aimed towards the realization of structural sizes not previously described in the literature. Only these large models did allow us to examine the low-frequency region of the vibrational density of states (VDOS). In this framework, we concentrated on developing efficient and computationally cheap procedures, which consequently required to make some compromises in the agreement achieved with experimentally determined structural properties. Nevertheless the criticism of NDM has to be taken seriously and we are pleased that they gave us the opportunity to examine how strong our findings on the low-frequency part of the VDOS depend on the quality of the model structure, in the sense of resemblance to experimental results for *a*-Si.

There is a second point to be mentioned. We wanted to study as far as possible with the same model electronic and phonon properties of *a*-Si.[6,7] This is why we were reluctant to use modified potentials, which might have given a bias into one or the other direction, and thus stayed with the original SW potential. The electronic density of states as well as the localized or extended nature of the eigenstates of our original model were investigated earlier by Knief, von Niessen, and Koslowski.[6] They found that there is no gap in the density of states but a mobility gap, which is the experimental finding. The states in the region of the Fermi level are localized for the less disordered structures, leading to the conclusion that these models in fact do *not* possess metallic electronic properties. Only the model with an unrealistic high amount of disorder has to be labeled an electronic conductor. There the gap region is filled up with states to such a degree that the states are delocalized.

The more disordered structures of our models do not display traces of crystallinity. This criticism of NDM is most likely based on the work of Wooten and Weaire,[4] who were detecting an imperfect amorphization of models relaxed with the Keating potential when they used a number of bond switches comparable to the ones in our models. But since we relax our models further into a local minimum of the Stillinger-Weber potential, we observe a considerable further displacement of the atomic positions. To assure this behavior, we were tracking several structural values, such as the average atomic displacements and energies during the relaxation process. Also, the detailed investigations of the local geometric distortions and their distribution within the structure were done. Together with the fact that the SW potential was originally designed to describe the fluid state of silicon as well, there is no serious danger of a return to the crystalline structure, bearing in mind that we perform the relaxation at zero temperature.

Let us discuss how it is possible to achieve an improvement of the structural properties of our model. We subsequently discuss the implications on the validity of the statements of our original paper.

 ©2002 The American Physical Society

There are two obvious approaches to improve the structural properties of our model. The first one consists in implementing a Metropolis Monte Carlo algorithm to perform a simulated annealing of the network. This is strongly demanded by NDM and what is normally done in the standard WWW bond-switching algorithm.[3,4] The problem connected with this procedure for our own studies is the immense computational cost that would severely limit the size of possible structures. To give an impression what kind of impact the simulated annealing has on the vibrational properties of the model, we show the VDOS of our ''wrong'' implementation of the WWW algorithm along with a ''correct'' implementation by Feldman, Allen, and Bickham[8] in Fig. 2(b). Both use the original SW potential. The difference is seen to be quite small up to about 500 cm^{-1}.

The other approach towards an improvement of the model is to replace the SW potential by a more sophisticated new empirical potential such as the environment-dependent interatomic potential (EDIP) (Refs. 9,10) or a ''modified'' version of the SW potential (mSW).[11] The use of the EDIP potential would imply a numerical approximation in calculating the force-constant matrix, because of the unavailability of an analytic form of the second derivative. Thus we believe that the use of the mSW potential is more convenient, when dealing with the vibrational properties. Moreover, it was shown that the use of the mSW potential leads to structures with a good reproduction of experimental findings. In Fig. 2(a), we compare the VDOS for crystalline silicon obtained with the help of the SW and the mSW potential, respectively. Herein the mSW potential shows a better agreement with the experimentally obtained spectrum.[12]

Consequently we perform investigations on the low-frequency vibrations of a-Si in analogy with our previous paper, but employing the mSW potential. Whenever we refer to the structures of our previously published paper, we call them SW models, whereas the new structures are labeled mSW models.

In contrast to our former studies we restrict our calculations with the use of the mSW potential to a single value of a bond-switching parameter of $c_n = 0.23$. This is sufficient for a detailed comparison with our previous results. A variation of the bond-switching parameter was only done at small system sizes of 4096 atoms. This was done to find the value of c_n giving the best overall reproduction of experimental results. The system size of the mSW model is 64 000 atoms as before.

The radial distribution function (RDF) is presented in Fig. 1. The RDF of our mSW model resembles the RDF of the SW model with $c_n = 0.20$, although there are some important improvements to note. First of all the third neighbor peak, a feature typical for the amorphous state, has almost totally vanished in the mSW model. Second, the small peak to the left of the second neighbor peak, a well-known artifact connected directly to the SW potential, has become a shoulder of the second neighbor peak if one uses the mSW potential. And last, there is now a true gap between the first and second neighbor peak of the RDF, which is not true for the SW model. We can state a very good agreement of the RDF of the mSW model with the experimental curve.[13–15]

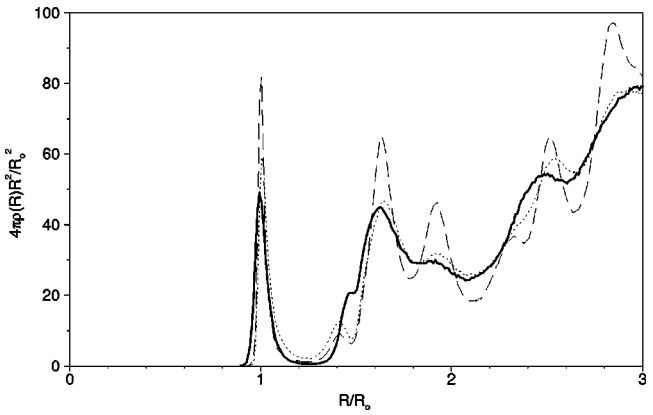

FIG. 1. RDF for different models of a-Si: bold line represents mSW model, $c_n = 0.23$; long dashed line represents SW model, $c_n = 0.15$; dotted line represents SW model, $c_n = 0.20$.

A view on the overall VDOS leads to similiar conclusions [Fig. 2(c)]. Again we find the closest correspondence between the results for the mSW model and the SW model with $c_n = 0.2$. The shape of the VDOS and the relative heights of the tranverse-acoustic and transverse-optical peaks substantiate this statement, while the absolute positions of the peaks differ. This is especially true for the transverse-optical peak, where the mSW model is in much better agreement with experiment.[12] This does not come as a surprise bearing in mind that the mSW potential was fitted to reproduce the experimental VDOS of a-Si. The changes in the tranverse-acoustic region are more subtle, the peak is somewhat broadened and shifted towards higher frequency for the mSW model. Since a broadening and a high-frequency shift tend to compensate each other if one focuses on the low-frequency range, it is not obvious from this figure, how the low-frequency vibrations are influenced by the change of potential. We will return to this question later.

We can also report on some investigations on the electronic properties of our mSW model.[16] The experimentally observed widths of the valence and conducting bands are well reproduced. There is no gap between these bands in the electronic density of states. This filling of the gap is caused by the defects present in the structure; it is in agreement with experiment. Yet the mSW model is no electronic conductor, since a mobility gap in the region of the Fermi level is present. Here the localization at the bottom of the conducting band is found to be stronger than at the top of the valence band. The absolute value of the width of the mobility gap is in a better agreement with experiment than it was found for the original SW model.

With respect to the RDF, VDOS, and electronic properties we can establish a perceptible though not dramatic improvement when switching from the SW to the mSW potential. This changes when one focuses on the two main shortcomings of the original SW model: the coordination defects and the bond-angle distribution. In Table I we list the percentages of coordination defects of the mSW model along with the values found for the SW models of our previous work. If we again compare to the SW model with $c_n = 0.2$, we can state a dramatic decrease of coordination defects for the mSW

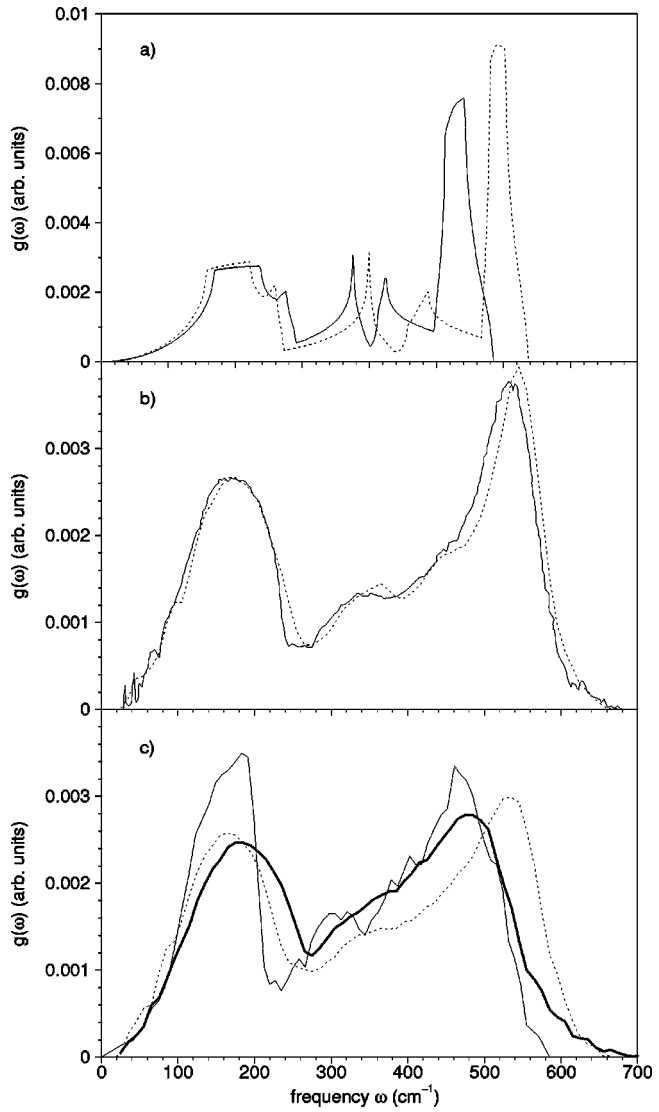

FIG. 2. Vibrational density of states $g(\omega)$ for several models. (a) Crystalline silicon; solid line represents mSW potential; dotted line represents SW potential. (b) *a*-Si, models with 4096 atoms; solid line represents ''correct'' implementation of the WWW algorithm with the use of the SW potential (from Ref. 8); dotted line represents SW model with $c_n=0.15$. (c) *a*-Si, models with 64 000 atoms; bold line represents mSW model, $c_n=0.23$; dotted line represents SW model, $c_n=0.20$; solid line represents experimental VDOS of *a*-Si (from Ref. 12). The two calculations involve 64 000 atoms up to 80 cm^{-1} and are continued to higher frequencies with 13 824 atoms.

model. Before we had 1.4% of threefold and 16.1% of fivefold coordinated atoms, now we have 4.4% of threefold and only 3.3% of fivefold coordinated defects. In agreement with existing literature the mSW potential favors undercoordinated Si atoms whereas the original SW potential strongly favors overcoordination to a degree, which is regarded as unrealistic. Looking at the overall defect concentration the mSW model resembles more closely the SW model with $c_n=0.15$ than the one with $c_n=0.20$. An average coordination number of 3.99 is obtained for the mSW model, which comes close to the results for the SW model with $c_n=0.1$ (4.02).

TABLE I. Percentage of coordination numbers found for the mSW model with $c_n=0.23$ and the SW models with varying bond-switching parameters c_n.

	mSW	SW			
$c_n=$	0.23	0.1	0.15	0.2	0.25
two-fold [%]	0.1			0.1	0.2
three-fold [%]	4.4	0.3	1.0	1.4	2.2
four-fold [%]	92.2	97.5	90.5	82.1	71.7
five-fold [%]	3.3	2.2	8.3	16.1	25.4
six-fold [%]			0.2	0.3	0.5
Average coordination	3.99	4.02	4.08	4.15	4.24

Similar conclusions apply to the average bond angle that is listed in Table II along with the standard deviation of the bond-angle distribution. Again the mSW model with an average bond angle of 108.9° comes closer to the ideal tetrahedron angle than the SW model with $c_n=0.15$. But more important, also the standard deviation of the bond-angle distribution for the mSW model is with a value of 12.7°, even smaller than the findings for the SW model with $c_n=0.15$.

When we compare the results of our mSW model with the experimental values for the defect concentration[17,18] (0.1 $-1.0\,\%$) and for the width of the bond-angle distribution[15] ($9.6-10.4°$), we have to admit that there is still some discrepancy. The presumably best current computer models for *a*-Si (Ref. 19) possess structural properties that are in these terms much closer to experiment. Therefore these models are more realistic than our mSW model, which lacks the step of a thermal annealing procedure as a sacrifice for an access to large structural models.

Nevertheless we believe that our calculations are justified. We achieve a good agreement with experiment regarding the RDF and the VDOS and many of the shortcomings of our old SW model are removed. Now let us see, if we can draw some conclusions from these tendencies on the effects in the low-frequency range of the VDOS.

In Fig. 3, we plot $g(\omega)/\omega^2$ versus frequency ω, where $g(\omega)$ is the VDOS. In this figure the frequency range is restricted to $\omega<300$ cm^{-1}. We also do not show any results for frequencies smaller than $\omega=10$ cm^{-1}, because the calculated $g(\omega)$ becomes unreliable for such small values.[1] For a comparison the curve for the mSW model is accompanied by the curves for the SW models and the SW crystal. There is an obvious similarity in the graphs for the mSW model

TABLE II. Average bond angle $\overline{\theta}$ and standard deviation of the bond-angle distribution $\sigma_{n(\theta)}$ for the mSW model with $c_n=0.23$ and the SW models with varying bond-switching parameters c_n.

	mSW	SW			
$c_n=$	0.23	0.1	0.15	0.2	0.25
$\overline{\theta}$	108.9°	109.1°	108.6°	108.0°	107.4°
$\sigma_{n(\theta)}$	12.7°	9.8°	13.3°	15.9°	18.3°

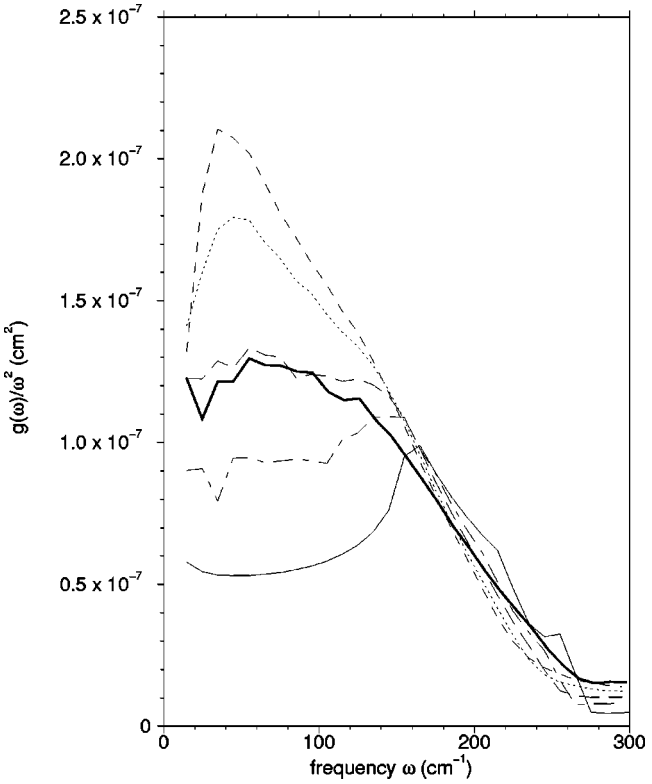

FIG. 3. Low-frequency part of $g(\omega)/\omega^2$ versus ω for the mSW model and the SW models for a-Si with a varying degree of disorder. Bold, mSW model $c_n=0.23$; solid, c-Si; dashed-dotted, SW model $c_n=0.1$; long dashed, SW model $c_n=0.15$; dashed, SW model $c_n=0.2$; dotted, SW model $c_n=0.25$.

and the SW model with $c_n=0.15$. The height of the plateau in $g(\omega)/\omega^2$ is somewhat reduced for the mSW compared to the SW model. Bearing in mind the resemblance of these two models regarding the defect concentration, it is evident that the latter plays a dominant role for the density of low-frequency vibrations. The type of defect does not seem to have much influence, noticing that for the mSW model threefold coordination and for the SW model fivefold coordination is the prominent defect-type. This independence of the vibrational properties on the defect-type was also found previously by the authors,[7] and holds as long as a potential with a natural cutoff of interaction is used.

Which consequences do these findings have for the validity of our previously published results on the origin of the boson peak in a-Si? Our SW model with $c_n=0.20$ has a realistic RDF and overall VDOS, but possesses an unrealistic high concentration of coordination defects. As the low-frequency VDOS is highly dependent on the defect concentration, it is clear that the peak in $g(\omega)/\omega^2$ is an artifact of the model. Still it remains valid that we have shown that a peak in $g(\omega)/\omega^2$ can be caused alone by disorder in the form of local geometric distortions without any anharmonic effects, albeit with an unrealistically high defect concentration.

Our previous paper clearly stated the existence of two phenomena that can be observed in the graph of $g(\omega)/\omega^2$ versus ω as the disorder is tuned to higher values. Besides the peak in $g(\omega)/\omega^2$ there is a general increase in the number of low-frequency modes, indicated by an upward shift of the plateau in $g(\omega)/\omega^2$ compared to the crystalline curve, which is parallel to the frequency axis. This effect was already found for our least disordered model with $c_n=0.10$. For the latter model we calculate a defect concentration of 2.5%, which is a value not too far from experimental findings and in the range of the best models available at present.

Since there is a strong dependence of the low-frequency VDOS on the coordination defect concentration, we expect that a model that on one hand is relaxed by simulated annealing and thus poor in coordination defects and on the other hand large enough to examine the low-frequency range of the VDOS, would presumably show an upward move of the plateau in $g(\omega)/\omega^2$ similar to the results for our SW model with $c_n=0.10$. It is then very likely that a large realistic but harmonic model of a-Si possesses additional low-frequency modes without disobeying the Debye ω^2 behavior.

To summarize, among our previously described effects of disorder on the low-frequency VDOS, the bump in $g(\omega)/\omega^2$ is presumably an artifact of the too high defect concentration of our models, whereas the increase of the low-frequency VDOS is likely to be observed also in more realistic large models of a-Si. Thus the main thought of our previous article persists: Already in the harmonic approximation an increase of the low-frequency VDOS over the crystalline value is observed. These additional states are only due to disorder and not due to anharmonic effects. They could be a part of an explanation of the boson peak.

ACKNOWLEDGMENTS

We thank Simone Knief for the calculation of the electronic properties of our models. F.F. would like to thank the Deutsche Forschungsgemeinschaft for financial support. Part of this work was also supported by the Fonds der Chemischen Industrie.

[1] F. Finkemeier and W. von Niessen, Phys. Rev. B **63**, 235204 (2001).
[2] S. M. Nakhmanson, D. A. Drabold, and N. Mousseau, Phys. Rev. B **66**, 087201 (2002).
[3] F. Wooten, K. Winer, and D. Weaire, Phys. Rev. Lett. **54**, 1392 (1985).
[4] F. Wooten and D. Weaire, Solid State Phys. **40**, 1 (1987).
[5] F.H. Stillinger and T.A. Weber, Phys. Rev. B **31**, 5262 (1985).
[6] S. Knief, W. von Niessen, and T. Koslowski, Phys. Rev. B **58**, 4459 (1998).
[7] F. Finkemeier and W. von Niessen, Phys. Rev. B **58**, 4473 (1998).
[8] J.L. Feldman, P.B. Allen, and S.R. Bickham, Phys. Rev. B **59**, 3551 (1999).
[9] M.Z. Bazant, E. Kaxiras, and J.F. Justo, Phys. Rev. B **56**, 8542 (1997).
[10] J.F. Justo, M.Z. Bazant, E. Kaxiras, V.V. Bulatov, and S. Yip,

Phys. Rev. B **58**, 2539 (1998).
[11] R.L.C. Vink, G.T. Barkema, W.F. van der Weg, and N. Mousseau, J. Non-Cryst. Solids **282**, 248 (2001).
[12] W.A. Kamitakahara, C.M. Soukoulis, H.R. Shanks, U. Buchenau, and G.S. Grest, Phys. Rev. B **36**, 6539 (1987).
[13] S.C. Moss and J.F. Gracyk, Phys. Rev. Lett. **23**, 1167 (1969).
[14] S. C. Moss and J. F. Gracyk, in *Proceedings of the 10th International Conference on the Physics of Semiconductors, Cambridge, 1970*, edited by S. P. Keller *et al.* (US AEC Division of Technical Information, Springfield, 1970), p. 658.
[15] K. Laaziri, S. Kycia, S. Roorda, M. Chicoine, J.L. Robertson, J. Wang, and S.C. Moss, Phys. Rev. B **60**, 13 520 (1999).
[16] S. Knief (private communications).
[17] M.H. Brodsky and R.S. Title, Phys. Rev. Lett. **23**, 581 (1969).
[18] S. Roorda, W.C. Sinke, J.M. Poate, D.C. Jacobson, S. Dierker, B.S. Dennis, D.J. Eaglesham, F. Spaepen, and P. Fuoss, Phys. Rev. B **44**, 3702 (1991).
[19] G.T. Barkema and N. Mousseau, Phys. Rev. B **62**, 4985 (2000).