PHYSICAL REVIEW B VOLUME 49, NUMBER 18 1 MAY 1994-II

Rapid Communications

Rapid Communications are intended for the accelerated publication of important new results and are therefore given priority treatment both in the editorial office and in production. A Rapid Communication in **Physical Review B** *should be no longer than four printed pages and must be accompanied by an abstract. Page proofs are sent to authors.*

Calculation of the three-particle contribution to the configurational entropy for two different models of amorphous Si

Orsolya Gereben, László Pusztai, and András Baranyai
Laboratory of Theoretical Chemistry, L. Eötvös University, Budapest 112, P.O. Box 32, H-1518, Hungary
(Received 12 January 1994)

The two- and three-particle contributions to the configurational entropy (S_2 and S_3, respectively) were calculated by the method of Baranyai and Evans [Phys. Rev. A **42**, 849 (1990)] for two different models of a-Si, obtained by reverse Monte Carlo simulations. The first model was the result of an unconstrained calculation, while the second one was obtained by using a constraint requiring 100% fourfold coordination. The pair-correlation functions of the two models were essentially the same, but cosine distributions of bond angles (a projection of the three-body correlation function) were remarkably different. Two-particle contributions to the configurational entropy do not differ for the two models. However, the difference in the three-particle contributions to the configurational entropy is large and the S_3 of the 100% fourfold coordinated model is much more negative than that of the unconstrained model. This work is an attempt to make a quantitative distinction between structural models with identical pair-correlation functions.

Recently it was shown[1] that quite different structural models of a-Si, generated by reverse Monte Carlo (RMC) simulation,[2] are equally consistent with given diffraction data.[3] The equal consistency involves highly similar, sometimes totally identical pair-correlation functions (PCF), $g(r)$, of different models. Qualitative distinction between models could be made through characteristics of local symmetries, such as the distribution of the number of neighbors, or the cosine distribution of bond angles (see, e.g., Ref. 4). It was not, however, possible to characterize the structural difference between models quantitatively. This was mainly beacause these *ad hoc* distributions cannot be linked to higher-order correlation functions trivially. The main objective of the present study is to find a proper means for the quantification.

The configurational entropy can be expanded as contributions from 2, 3,...,N body correlations, and it was also possible to derive an ensemble invariant form of this expansion.[5] This effectively means that it is possible to approximate the total configurational entropy by calculating the two-[5] and three-body[6] contributions from sets of particle coordinates (configurations). The configurations can be results of any computer simulation, for instance, of RMC. In the case of our models of a-Si it is expected that the constrained model would give a larger negative three-body contribution (S_3) than the unconstrained one, whereas the two-body contributions (S_2) from these two models should be equal.

The calculation of S_3 necessitates the calculation of the three-particle correlation function. This is rather cumbersome and extremely time consuming because of the large number of configurations needed for acceptable statistics. Probably this is why the method is not applied more widely. Nevertheless, we have attempted the evaluation of S_2 and S_3 for two large models since the difference expected to be found in S_3 promised the quantitative measure that we were looking for.

First, sufficiently large samples, i.e., a sufficient number of particle configurations, had to be collected by reverse Monte Carlo simulation. The technique has been described in detail elsewhere.[2,7] In short, according to the RMC algorithm particles are moved around in order to achieve the best agreement with a given (set of) experimental, mostly diffraction, data. In addition to the data, different constraints can be imposed, such as those on coordination numbers or on bond angles,[3] according to our previous (chemical) knowledge of the structure. As a result of RMC, particle configurations (sets of Cartesian coordinates of all the particles in the system) are obtained that are consistent with the experimental data. These configurations can be used later for geometrical analyses. Methods for characterizing the local structure are described in Ref. 4. The calculation of S_2, and particularly of S_3 would be a different application of the configurations resulting from RMC.

A total of four RMC calculations were completed, forming two unconstrained-constrained pairs. One pair of models (sample 1 and sample 2, as unconstrained and constrained, respectively) contained 216 Si atoms per configuration, whereas the other pair (sample 3 and sample 4, in the same order as above) contained 1728 atoms. The number density was always 0.05 Å^{-3}. Sample 1 con-

0163-1829/94/49(18)/13251(4)/$06.00

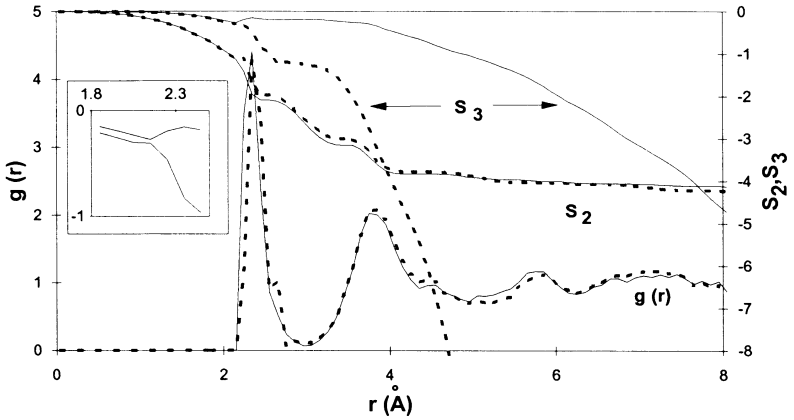

FIG. 1. Pair-correlation functions, and two- and three-particle contributions to the configurational entropy, S_2 and S_3, for samples 1 and 2 (216 Si atoms per configuration). (Solid curves: sample 1; dashed curves: sample 2.) The inset shows for emphasis an enlargement of a characteristic qualitative difference between S_3 curves of unconstrained and constrained structures. (Upper curve: sample 1; lower curve: sample 2.)

sisted of 100 independent configurations with no additional constraint applied when fitting to the structure factor of Kugler *et al.*[3] Sample 2 contained 100 independent configurations that were generated while 100% fourfold coordination was required, and fitted to the *pair-correlation function* $g(r)$ calculated over the 100 configurations of sample 1. Sample 3 was built in the same way as sample 1 except that the number of particles was increased to 1728. Sample 4 consisted of 100 configurations collected by RMC applying 100% fourfold coordination constraint and fitting, again, to the *structure factor* $S(Q)$ of Ref. 3.

In Fig. 1 the PCF's, as well as S_2's and S_3's calculated for samples 1 and 2 are shown. During the entropy calculation a resolution of $\Delta r = 0.1$ Å was applied. While the PCF's and the S_2's are practically the same for the two samples, i.e., the structure does not differ at the two-particle correlation level, the S_3's already differ remarkably after the first coordination sphere. At higher r values the two S_3 curves diverge greatly, S_3 for sample 2 (100% fourfold coordination) being much more negative. Also, the S_3 function for sample 2 is more structured than for sample 1. Note also the qualitative difference in the S_3 curves around the first peak of $g^{(2)}$ (see inset of Fig. 1): S_3 for the unconstrained structure has a minimum at about 2.1 Å, while for the constrained structure S_3 decreases monotonically.

As can be seen from Fig. 1, S_2 changes only slightly after about $r = 4.5$ Å, i.e., after the second peak of $g(r)$. This means that the two-particle correlations are so small above that value that they do not give rise to any contribution to S_2.

As was shown in Ref. 6, S_3 can be considered converged if the curve reaches its terminal flat plateau and does not decrease any longer. This status would be connected to the distance(s) where there is no more correlation in the positions of three particles, that is, where $g^{(3)}(r_1, r_2, r_3)$ oscillates to a lesser extent than $g^{(2)}(r)$ above 4.5 Å, in our case. One would expect that this happens at no larger distances than for $g^{(2)}(r)$ (and consequently, S_2). This would also be logical since in general, higher-order correlations are known to be more short-ranged than lower correlations. In practice, however, S_3 always seems to diverge, and the generic cause for that lies in the finiteness of the sample on which $g^{(3)}$ is calculated. When evaluating $g^{(3)}$ for such a sample, the situation at large r is much worse, compared to that at low r, although the volume elements are increasing as functions of interparticle distances. Furthermore, it should be noted that the integration algorithm[6] cannot separate real oscillations from statistical fluctuations, that is, both give rise to contributions to S_3 (and also to S_2). This is why the extrapolation technique of Ref. 6 had to be implemented, even for rather disordered systems.

In light of the above, it is now possible to interpret the behavior of S_2 and S_3 for samples 1 and 2 (Fig. 1). S_2, according to the good statistical accuracy of $g^{(2)}$, is convergent. S_3, due to the poor statistics at higher r, diverges (steadily decreases) for both samples. However, the divergence of S_3 for sample 2 is enormous, partic-

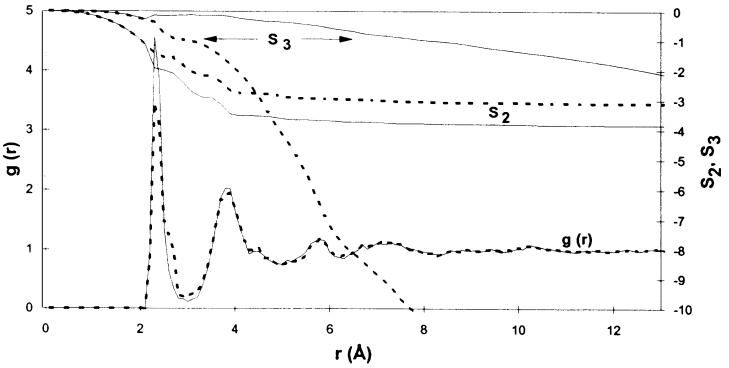

FIG. 2. Pair-correlation functions, and two- and three-particle contributions to the configurational entropy, S_2 and S_3, for samples 3 and 4 (1728 Si atoms per configuration). (Solid curves: sample 3; dashed curves: sample 4.)

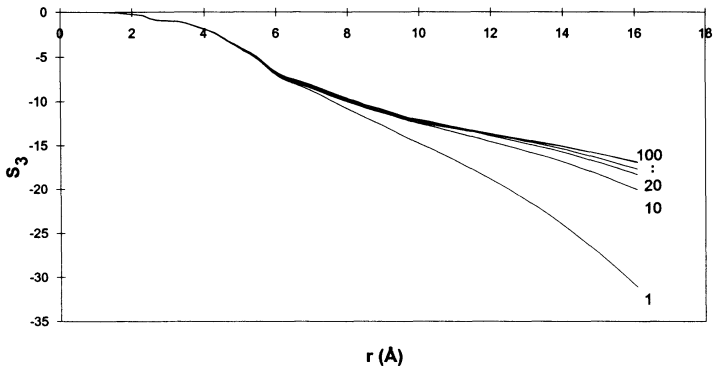

FIG. 3. Three-particle contribution to the configurational entropy, S_3, calculated over 1, 10, 20, 30, 70, and 100 configurations. Note that the curves for 70 and 100 configurations are merged.

ularly if we consider that the sizes of the samples were identical. Thus the *difference* between S_3's of the two structures, which is precisely what we are looking for, cannot be considered as merely an artefact of the statistics, but it does have strong structural origin.

Samples 3 and 4 represent considerably larger systems, so that calculations at this scale cannot be carried out routinely yet. A value of 0.2 Å was chosen for Δr in samples 3 and 4 so that the effects of statistical uncertainities should be much smaller. As is evident from Fig. 2, there is a slight difference between the PCF's, particularly around the first peak, and this deviation also shows up in the S_2's. The asymptotic value of S_2 for sample 3 is a greater negative value than that for sample 4, by about 25%. However, the difference between S_3's of the unconstrained (sample 3) and constrained (sample 4) configurations is already larger than a factor of three (i.e., 300%), in the first coordination sphere. At higher r values it becomes enormously large, just as in the case of the smaller systems.

It is useful to compare the corresponding unconstrained (samples 1 and 3) and constrained (samples 2 and 4) systems, since up to the limitations of the smaller systems (i.e., up to about 8 Å) they should behave rather similarly. The effect of better statistics can be noticed already on the asymptotic values of S_2: for the smaller systems (and at the same time, of finer r resolution) these values are consistently greater then for the larger systems, where the resolution was coarser, as well. The minimum difference is about 10%, between samples 1 and 3. Better statistics of sample 3 reduced the value of S_3 to less than half, compared to sample 1. Roughly the same ratio applies for the other pair as well. It should be noted that the S_3 values calculated up to about 3.5 Å, where relatively well-defined plateaus can be found in all cases, show hardly any dependence on system size or on r spacing. On the basis of this finding, it is suggested that if what is required is not the calculation of the total configurational entropy, but only a measure for characterizing different degrees of structural order that correspond to identical pair correlations, then S_3 could be truncated at an appropriate value of r. This sensible r value has to be well over the first maximum of $g^{(2)}$ in order to assure us that the main contribution from $g^{(3)}$ to S_3 is accounted for.

In samples 1 and 3 the main part of the entropy comes from the two-particle contributions, whereas in samples 2 and 4 the S_3 exceeds S_2 at an early stage, after the second coordination sphere. Since S_3 for the similar systems behaves consistently and qualitatively similarly, it is obvious that there is a structural basis for this. However, from earlier experience[6,8] it seems unlikely that S_3 would so greatly exceed S_2. This phenomenon might have something to do with the nature of the systems of samples 2 and 4, namely, with the way they were constrained. Such a stiff coordination constraint, which holds a covalentlike network together, may restrict the explorable volume of the phase space, which is attributed to the given system, in a finite period of time. This would effectively mean that whatever the number of configurations (i.e., phase-space points, in this terminology) that could be sampled, they would be too close to each other. Therefore averages taken over them that are sensitive to statistics would not be representative of the system. This kind of nonergodic behavior, known as bottlenecks in Monte Carlo terminology, could be responsible for the seemingly irrational behavior of the S_3's of samples 2 and 4. Note that this behaviour, achieved through a computer code, is remarkably similar to what happens to an amorphous covalent network in reality.

The validity of this sort of reasoning should be properly checked. The testing procedure should involve sampling of an extremely large number of configurations, at least one or two orders of magnitude larger than the present samples. Therefore the costs for this calculation are at the moment prohibitive. The behavior of S_3 as a function of N, the number of configurations, can be investigated up to N=100, and that is given by Fig. 3 for sample 4. There is a large improvement between the calculations over 1 and 10 configurations, but after 70 configurations the change is negligible. It is important to collect some configurations, purely for better statistics, but it is useless to exceed a relatively small number.

Summarizing the differences in the three-particle contribution to the total configurational entropy, S_3, found for systems with identical (samples 1 and 2), or near identical (samples 3 and 4) pair correlations, qualitative, as well as quantitative description can be given. Qualitatively speaking, S_3 for the constrained systems (samples 2 and 4) greatly overshot S_2, whereas for the unconstrained structures S_3 was only half (sample 3) of S_2. This is fundamental, even if the total difference proba-

bly cannot be attributed to structural differences. The qualitative difference in the shape of S_3 curves around 2 Å (see inset of Fig. 1, as well as Fig. 2) is also consistent and rather characteristic, although it could not yet be fully interpreted. It is clear that the behavior of the unconstrained systems resemble that of simpler disordered systems.[6,8] Quantitatively, S_3 of the constrained structures calculated up to 3.5 Å, whose value served as a good reference distance where all four systems were comparable, was consistently a negative value about three times greater than S_3 for the unconstrained structures. All these characteristics are consistent with the fact that the constrained systems have more ordering in their structures, and therefore their configurational entropy should be less than that of the unconstrained systems.

There seem to be great potentialities in calculating S_3 for shorter distances, such as up to the second minimum of the PCF. This can be done routinely, and the results of these calculations bear all the characteristics of much larger, longer ranged samples. This, it is believed, opens up new routes for characterizing structural differences quantitatively.

This work has been supported by OTKA Grants No. F 4320 and No. F 7218.

[1] O. Gereben and L. Pusztai (unpublished).
[2] R.L. McGreevy and L. Pusztai, Molec. Sim. **1**, 359 (1988).
[3] S. Kugler, L. Pusztai, L. Rosta, P. Chieux, and R. Bellisent, Phys. Rev. B **48**, 7685 (1993).
[4] R.L. McGreevy and L. Pusztai, Proc. R. Soc. London, Ser. A **430**, 241 (1990).
[5] A. Baranyai and D.J. Evans, Phys. Rev. A **40**, 3817 (1989).
[6] A. Baranyai and D.J. Evans, Phys. Rev. A **42**, 849 (1990).
[7] R.L. McGreevy, M.A. Howe, D.A. Keen, and K. Clausen, in IOP Conf. Proc. No. 107 (Institute of Physics and Physical Society, London, 1990), p. 165.
[8] A. Baranyai and D.J. Evans, Z. Naturforsch. Teil A **46**, 27 (1991).