Configurational Entropy of Network-Forming Materials

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We present a computationally efficient method to calculate the configurational entropy of network-forming materials. The method requires only the atomic coordinates and bonds of a single well-relaxed configuration. This is in contrast to the multiple simulations that are required for other methods to determine entropy, such as thermodynamic integration. We use our method to obtain the configurational entropy of well-relaxed networks of amorphous silicon and vitreous silica. For these materials we find configurational entropies of $0.93k_B$ and $0.88k_B$ per silicon atom, respectively.

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In materials such as vitreous silica, amorphous silicon, or vitreous ice, the structure is determined by the set of bonds (covalent or hydrogen) between particles. In this manuscript, we will refer to these materials as *network-forming materials*. While the local environment of each particle is usually governed by strict rules, the bonded network can show a wide variety of different topologies. The focus of this work is to present a method to estimate the number of topologies that a network-forming material can take, or more precisely, its configurational entropy.

The common computational procedure to estimate the entropy S at temperature T_2 is to measure the energy E as a function of temperature and then to integrate from a temperature T_1 at which the entropy is known:

$$S(T_2) - S(T_1) = \int_{T_1}^{T_2} \frac{1}{T}\frac{\partial E}{\partial T}\,dT. \quad (1)$$

This requires sampling a large number of different networks, and can therefore be applied only to systems with fast dynamics. In this work, we present a completely different approach to estimate the entropy, based on information theory [1], and related to the work of Schlijper *et al.* who determined the entropy of the Ising and three-states Potts models [2].

One important concept in information theory is the Shannon entropy. It is commonly explained in the context of a string of n bits. In this case, the Shannon entropy $H(n)$ is defined as

$$H(n) = -\sum_i p(i)\log_2 p(i), \quad (2)$$

where the index i runs over all possible bit sequences of length n and $p(i)$ is the probability of sequence i occurring. A related concept is the entropy density s of a large string of N bits:

$$s = \lim_{n\to\infty}[H(n+1) - H(n)]. \quad (3)$$

A practical procedure to estimate s for such a long string is to extract from it a large number m subsequences, each containing n bits with $n \ll N$. An estimate for the probabilities $p(i)$ is then given by

$$p(i) \approx \frac{f_i}{m}, \quad (4)$$

where f_i equals the number of times subsequence i was observed. The estimates for $p(i)$ in combination with Eq. (2) yield $H(n)$. The entropy density s is then obtained using Eq. (3). Usually, the limit $n \to \infty$ converges rapidly and even moderate values of n are sufficient to predict s accurately.

For systems in equilibrium it is easily shown that the Shannon entropy and the thermodynamic entropy of Eq. (1) are equivalent, apart from a factor of ln(2). In this case, the probabilities $p(i)$ are simply the Boltzmann weights: $p(i) = \exp(-\beta E_i)/Z$, where β is the inverse temperature, Z the partition function, and E_i the energy of state i. In the present work we show how information theory can also be used to obtain the configurational entropy of network-forming materials. The method we present can be applied to any network provided (i) the atomic coordinates are known and (ii) a list of bonds is supplied or can be constructed—for instance based on a distance criterion—which uniquely determines the network.

To determine the configurational entropy of a network-forming material we choose a large number m of random positions in the simulation cell. For each position we find the nearest n particles and identify the graph formed by the bonds connecting these particles. We then assign a label to this graph, based on the graph automorphism [3]: different labels are assigned to sets of atoms with different bonding topologies, while a renumbering of the atoms does not yield a different label. We count the number of times a graph is observed and use Eq. (4) to estimate its corresponding probability of occurrence. These probabilities are fed into Eq. (2) to obtain $H(n)$.

A small displacement of one of these random positions will usually result in exactly the same list of n nearest particles and thus the same graph. Consequently, there is an upper bound to the number m of random positions that one should choose in a simulation cell containing N particles. An estimate of this upper bound is obtained from the typical distance over which a random position can be displaced without altering the selected graph. From this we obtained as upper bounds $m = 1.6nN$ and $m = 3.4n^2N$ for two-dimensional and three-dimensional networks, respectively.

A related side effect of choosing random positions is that the number of different graphs observed gets multiplied with a factor proportional to n^{d-1}. This results in a correction to $H(n)$ of the form $g(n) = (d - 1)\ln(n)$, with d the spatial dimension of the network. The latter can be verified in crystalline networks where the configurational entropy is zero.

Graphs with a probability $p(i)$ smaller than $1/m$ will likely be observed only once, if at all. This finite-size effect grows with n, when the selected graphs become very complex. To monitor the impact of this effect, we record the quantity $H_1(n)$, defined as the contribution to $H(n)$ of the topologies observed once. We reject the measurements for which $H_1(n)$ exceeds 1% of $H(n)$. Furthermore, we observed that the quantity $H(n) + c \cdot H_1(n)/H(n)$ converges much faster with increasing m than $H(n)$ itself, with a suitable choice of c. We therefore use this extrapolated value as our best estimate for $H(n)$.

In Fig. 1 we show the typical behavior of the corrected Shannon entropy $H_c(n) \equiv H(n) - g(n)$ as a function of graph size n. The entropy follows from Eq. (3). The rapid convergence of the limit is demonstrated by the linear behavior of $H_c(n)$ for intermediate n shown in Fig. 1 by the dashed line. The entropy per atom equals the slope of this line. In Fig. 1 we have marked with circles the points for which $H_1(n)$ exceeds 1% of $H(n)$. These points suffer from finite-size effects and should not be used.

To test the usefulness of the above procedure, we apply it to the *sillium* model [4], one of the prototype models to study network-forming materials. In this model, tuned for amorphous silicon, an explicit list of covalent bonds between pairs of Si atoms is kept, with the property that each Si atom is bonded to four neighboring atoms. The energy is described by the Keating potential, which contains a quadratic penalty for bond-length deviations from the crystalline distance of 2.35 Å, and a quadratic penalty for bond-angle deviations from the tetrahedral angle $\Theta_0 = \arccos(-1/3)$. The list of bonds determines the atomic positions uniquely, since in this model the energy is minimized at all times. As a result, the phase space of this model is limited to a finite number of $3N$-dimensional points. The evolution of the network consists of a large number of random bond transpositions, each accepted with the Metropolis probability:

$$P = \min\left[1, \exp\left(\frac{E_b - E_f}{k_B T}\right)\right], \tag{5}$$

where T is the temperature and E_b and E_f are the total (minimized) energies of the system before and after the proposed bond transposition. A typical sillium network is shown in Fig. 2. Our networks are generated as described in Refs. [5,6], in which a number of algorithmic improvements have been proposed as compared to the original algorithm of Wooten, Winer, and Weaire.

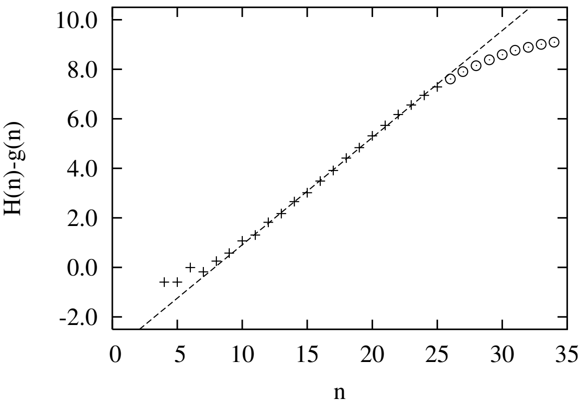

FIG. 1. Typical behavior of the corrected Shannon entropy $H_c(n)$ in units of k_B as a function of graph size n; crosses (circles) mark measurements for which $H_1(n)$ contributes less (more) than 1% to $H(n)$. The dashed line is a straight-line fit to the crosses, starting from $n = 10$. The slope of this line is our estimate for the configurational entropy per atom s. These data are obtained from a two-dimensional sillium configuration containing 20 000 atoms.

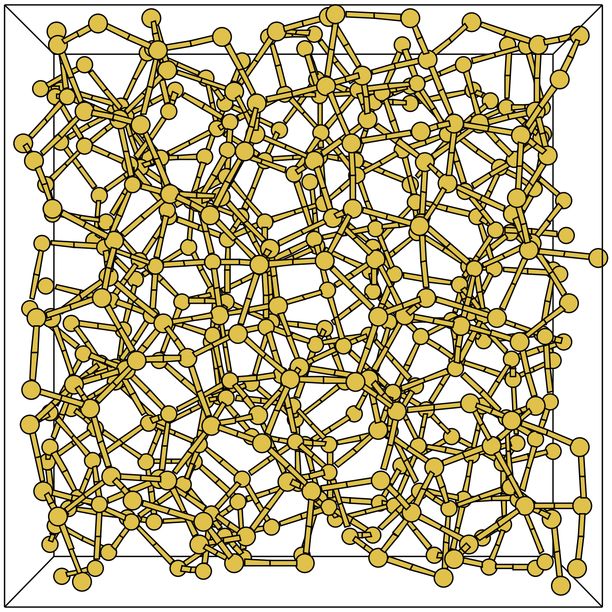

FIG. 2 (color online). A three-dimensional sillium network. Each particle is fourfold coordinated but no long-range order exists.

To verify the validity of the information theory approach we first turn to a two-dimensional version of the sillium model. Contrary to the three-dimensional sillium model, the dynamics here does not lead to glassy states. This allows us to determine the entropy in equilibrium using both the standard approach—via Eq. (1)—as well as information theory. In this two-dimensional model, atoms are threefold coordinated and the ideal bond angle is 120°; a typical configuration is shown in Fig. 3.

We simulate a two-dimensional sillium network containing 1008 atoms for a number of (physically interesting) temperatures ranging from $k_BT = 0.15$ eV to $k_BT = 0.60$ eV using periodic boundary conditions in both directions. At each temperature we bring the system to equilibrium with 100 attempted bond transpositions per atom. Next, 20 snapshots of the network are stored; each separated by five attempted bond transpositions per atom. From these snapshots the average energy and the Shannon entropy are obtained. In determining the Shannon entropy we draw clusters from each snapshot simultaneously. After the simulation has covered the entire temperature range, the entropy is also obtained from the average energy measurements and Eq. (1).

Figure 4 shows the configurational entropy as a function of temperature where the standard thermodynamic approach is compared to information theory. There appears to be a phase transition near $k_BT = 0.37$ eV shown by the sudden jump in entropy. The remarkable feature of the displayed results is the overall good agreement between the two methods, even near the phase transition. This is in agreement with related work on the Ising model [2], in which also surprisingly little numerical problems were encountered close to the critical point.

Next, we use information theory to determine the configurational entropy of a well-relaxed three-dimensional sillium network containing 20 000 atoms. This network was generated using the improved Wooten, Winer, and Weaire algorithm [5,6]. The Keating energy of this network is 0.286 eV per atom; the standard deviation in the mean bond angle is 9.63°. Structural and electronic properties of this network are in excellent agreement with experimental properties of amorphous silicon [6]. Applying our method to this model, we obtain a configurational entropy of $0.93k_B$ per atom.

By construction, *sillium* networks do not contain coordination defects. To study the effect of defects, we generated a number of networks in which coordination defects were introduced by removing from the explicit list of bonds the longest ones. The method works equally well for such networks in which the atomic coordination number varies significantly. We observed that, as long as less than 2% of the atoms are undercoordinated, the configurational entropy does not change significantly.

The (classical) vibrational entropy is obtained from the eigenvalues of the dynamical matrix and for this network was found to be $3.07k_B$ per atom. For the crystalline phase the configurational entropy is zero and only the vibrational entropy contributes to the entropy, in this case $3.18k_B$ per atom. The difference in entropy between the crystalline and amorphous phases of silicon is therefore estimated to be $0.82k_B$ per atom.

The energy difference between the crystalline and amorphous phases of silicon was recently determined by Biswas [7] using tight binding, who found an energy difference of 0.18 eV per atom which is in good agreement with values reported in Ref. [8].

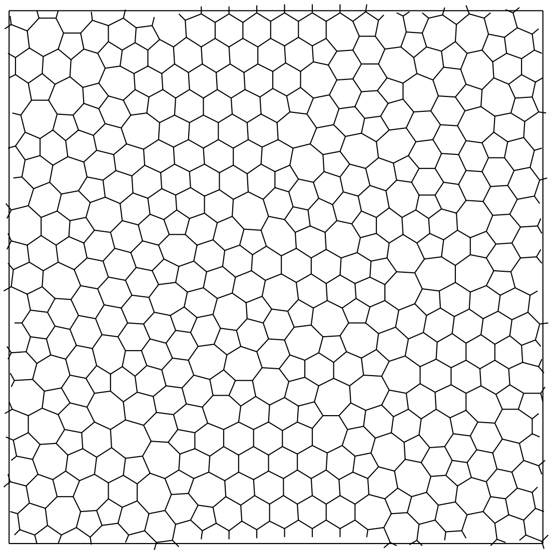

FIG. 3. A two-dimensional sillium network. Each particle is threefold coordinated, with a preferred bond angle of 120°.

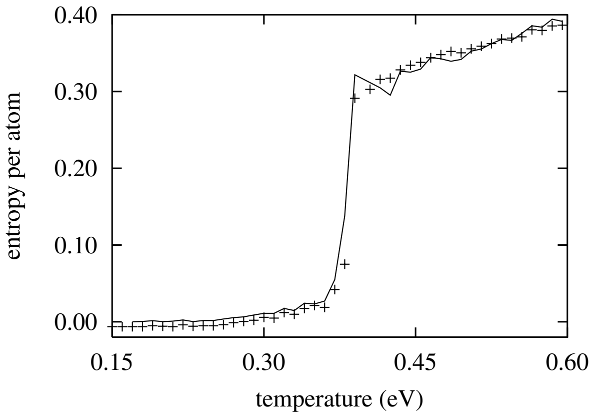

FIG. 4. Diagram showing the configurational entropy per atom in units of k_B as a function of temperature in eV for a two-dimensional sillium network consisting of 1008 atoms. The solid curve shows the entropy per atom as obtained using the standard thermodynamic approach; crosses show the entropy per atom obtained using information theory.

With the above estimates for the differences in energy and entropy we can calculate the transition temperature T_c, defined as the temperature where the free energy difference between the crystalline phase and the amorphous phase changes sign. It is given by

$$T_c = \frac{\Delta E}{\Delta S}, \tag{6}$$

where ΔE and ΔS are the energy difference and the entropy difference between the crystalline and the amorphous phase, respectively. Substitution of our estimates for ΔE and ΔS into Eq. (6) yields $T_c \approx 2547$ K. This temperature compares remarkably well with the value of $T_c \approx 2500$ K as inferred from calorimetric experiments [9], and is well above the melting point of silicon. It confirms that the amorphous phase is not thermodynamically stable at any temperature.

As a final application of our method we determine the configurational entropy of vitreous silica. The structure of this material is formed by covalent bonds between silicon atoms and oxygen atoms. Barring rare defects, each silicon atom is bonded to four oxygen atoms and each oxygen atom is bonded to two silicon atoms. We generate a silica network containing 3000 atoms (with periodic boundary conditions) in a spirit similar to amorphous silicon, but we replace the Keating potential by the one of Tu and Tersoff [10,11]. The resulting network is then quenched with the more realistic BKS potential [12], using parameters as described in Ref. [13]. The BKS energy per silicon atom of the quenched network is 0.13 eV above that of the β-cristobalite structure. For comparison, samples prepared by molecular dynamics typically yield a much larger energy difference of 0.30 eV. This clearly demonstrates that our network is well relaxed. After quenching with the BKS potential, the atoms remain perfectly coordinated: the silicon-oxygen bonds are easily reconstructed from a distance criterion and the silicon-oxygen radial distribution function. For our network, the average O-Si-O bond angle is 109.43° with a standard deviation of 4.40°; the average Si-O-Si bond angle was found to be 150.85° with a standard deviation of 12.09°.

To estimate the configurational entropy per silicon atom in well-relaxed vitreous silica, we used the above network and replaced each oxygen atom plus its two bonds by a single silicon-silicon bond. Next, we applied the information-theoretic method described earlier on this network and found for the configurational entropy $0.88k_B$ per silicon atom. Given the limited size of this sample we estimate that the actual entropy might be up to 10% larger. Ignoring the difference in vibrational entropy, as well as the entropy contribution of possible multiple oxygen positions, we obtain for the transition temperature of vitreous silica $T_c \approx 1700$ K.

In summary, we have developed a computationally efficient method to determine the configurational entropy of network-forming materials. For well-relaxed samples of amorphous silicon and vitreous silica, we find for the entropy per silicon atom $0.93k_B$ and $0.88k_B$, respectively. In future research, we hope to extend the applicability of this method to other disordered materials such as colloidal systems and metallic glasses.

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