Reasonable and robust Hamiltonians violating the third law of thermodynamics

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It has recently been shown that the third law of thermodynamics is violated by an entire class of classical Hamiltonians in one dimension, over a finite volume of coupling-constant space, assuming only that certain elementary symmetries are exact, and that the interactions are finite ranged. However, until now, only the existence of such Hamiltonians was known, while almost nothing was known of the nature of the couplings. Here we show how to define the subvolume of these Hamiltonians—a ''wedge'' W in a d-dimensional space—in terms of simple properties of a directed graph. We then give a simple expression for a specific Hamiltonian $\mathcal{H}^*$ in this wedge, and show that $\mathcal{H}^*$ is a physically reasonable Hamiltonian, in the sense that its coupling constants lie within an envelope that decreases smoothly, as a function of the range l, to zero at $l=r+1$, where r is the range of the interaction. [S1063-651X(97)00712-5]

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I. INTRODUCTION

It is sometimes stated [1] that all materials in their lowest-energy states are perfect crystals, i.e., that matter at zero temperature is characterized by periodic order of the atoms. If this is true, it follows that disorder persisting to low temperatures, in amorphous solids for example, must be interpreted as a result of trapping of the system in a metastable state. Another consequence is that the third law of thermodynamics holds in the Planck form [2,3], which states that the entropy density tends to zero as the temperature $T\to 0$.

These statements, however plausible [4], have not been proved [5]. One might aim to prove that any physically reasonable microscopic Hamiltonian describing a material has a unique ground state that is spatially periodic. More generally, one wishes to know the minimal conditions on the Hamiltonian sufficient to guarantee a periodic ground state. Both problems are unsolved in general, but some progress has been made, particularly for one-dimensional systems [3]. Radin and Schulman [6] showed that if attention is restricted to a one-dimensional system of interacting classical units (''spins''), each of which can exist in a finite number k of distinct states, with no interactions beyond a spatial range r, then there exists a ground state that is periodic with period at most k^r. In particular, if the ground state is nondegenerate then it has perfect periodic order.

Thus, in this class of model systems, disorder can occur only if the ground state is degenerate. This result can be strengthened by the observation that degenerate ground states occur only ''rarely,'' in the sense that they require fine tuning of the system's parameters (coupling constants) to precise values [3,7,8]. In other words, degeneracy occurs only on a set of measure zero in the space of Hamiltonians. In the absence of accidental degeneracies, then, Radin and Schulman's result implies that the ground state of such a discrete classical system is always periodic.

Recently, however, Canright and Watson [8] (CW) have shown that this picture must be modified if the system is constrained by an exact symmetry. The idea that symmetry can imply degeneracy is familiar. For the discrete classical chain, CW showed that, under suitable circumstances, the degeneracy arising from symmetry can result in a nonzero entropy density, throughout a finite volume of the space of coupling parameters. In this phase, termed a D-pair phase, almost all the ground-state configurations are aperiodic. The D-pair phase is robust in the sense that it is not sensitive to small perturbations in the coupling constants defining the Hamiltonian, as long as these perturbations respect the symmetry and the restriction to interactions of range r. It is also sufficiently robust to persist to finite temperatures.

CW considered two symmetries in detail: spatial inversion (I), and spin inversion (S). They showed rigorously that, for S symmetry, D-pair phases exist if and only if k is odd, while for I symmetry, they exist for $k\geqslant 3$ and $r\geqslant 2$. The Ising $(k=2)$ case is exceptional in that D-pair phases occur with I symmetry only for range $r\geqslant 5$.

Although the CW proof is constructive in the sense that it provides a method for finding all possible D-pair configurations for given k and r, there are immediate open questions. The CW result establishes the existence or nonexistence of D pairs in each case, but gives no information on the characteristics of the region in the phase diagram (the space of coupling parameters) occupied by the D-pair phase, when it exists—except that it has finite volume. One would like to know the size and location of the D-pair region. The location is important, since D-pair phases are of little interest unless they occur in a physically reasonable part of the phase diagram. For example, consider a Hamiltonian whose coupling constants increase with spatial separation, and then drop to zero beyond the cutoff range r. We consider such a Hamiltonian to be ''unphysical.'' Conversely, if the D-pair region includes Hamiltonians whose couplings decrease smoothly as a function of interaction range l, reaching zero at $l=r+1$ (or before), then we would claim that the case has been made that physically reasonable Hamiltonians can give ground states violating the third law.

In this paper we investigate these questions. After Sec. II, which reviews the formalism used in the construction of D

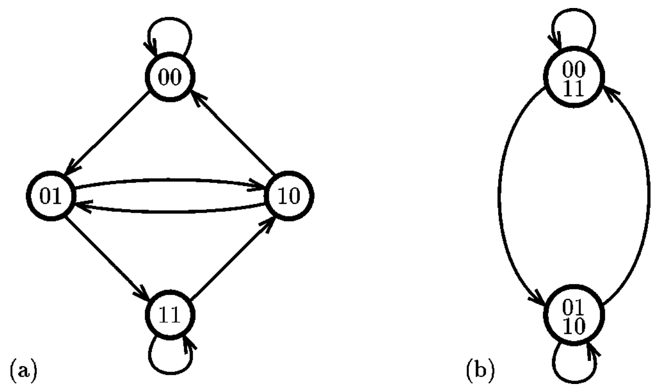

FIG. 1. (a) The graph $G_2^{(2)}$. Configurations of a spin chain correspond to infinite paths in the graph, and possible ground states correspond to simple cycles. (b) The symmetry-reduced graph ${}^S G_2^{(2)}$, obtained from (a) by identifying nodes and arcs which are equivalent under spin-inversion (S) symmetry.

pairs, we derive in Sec. III results that characterize the geometry of the D-pair region in terms of the combinatorial properties of the corresponding graph cycles. In Sec. IV, we provide a simple construction for writing down an explicit Hamiltonian corresponding to any given D-pair. We prove that this Hamiltonian has couplings that fall off approximately linearly with distance, which shows that it is indeed possible to have D-pair phases without pathological Hamiltonians.

II. GRAPHS, CORRELATION POLYTOPES, AND *D* PAIRS

The system of interest is composed of interacting classical units, forming an infinite one-dimensional chain. Each ''spin'' σ_i can take k distinct values, which we label $0,1,\ldots,k-1$. A general Hamiltonian having interactions of maximum range r can be written as

$$H=\sum_i f(\sigma_i,\sigma_{i+1},\ldots,\sigma_{i+r}), \tag{1}$$

where the sum is over all sites. Our interest is in ground states of H, which are those configurations $\{\sigma_i\}$ that minimize the energy density in the thermodynamic limit, i.e., $\mathcal{H}\equiv H/N$ with the number of sites $N\rightarrow\infty$. In particular, we seek ground states that do not require fine tuning of coupling parameters to precise values; hereafter we restrict the term ground state to mean minimum-energy states that are robust with respect to small changes in the Hamiltonian. (A more precise definition in this context is given in Ref. [8].)

It is very useful to represent the Hamiltonian pictorially as a directed graph $G_r^{(k)}$ with energy weights assigned to the arcs [3,7–9]. An example, with $k=2$ and $r=2$, is shown in Fig. 1(a). The graph has k^r nodes, each representing a possible sequence of r spins in the system. The arcs in the graph correspond to the operation of spatial translation in the chain by one unit: a directed arc connects two nodes if the rightmost $r-1$ spins of one agree with the leftmost $r-1$ spins of the other. The arc pointing from the node $(\sigma_0,\sigma_1,\ldots,\sigma_{r-1})$ to the node $(\sigma_1,\sigma_2,\ldots,\sigma_r)$ is assigned an energy weight $f(\sigma_0,\sigma_1,\ldots,\sigma_r)$. Any spin configuration of the chain is represented by an infinite path in the graph, and its energy density equals the average weight of the arcs in the path: $\epsilon=E/N=\Sigma_\sigma f(\sigma)n_\sigma$, where n_σ is defined as the average occurrence of an arc σ in the path. Thus, each spin configuration is characterized by its arc densities $\{n_\sigma\}$. The arc densities are not all independent, since they satisfy flow constraints [7] that state that at each node the sums of incoming and outgoing arc densities are equal. In addition, they satisfy the inequalities $0\leqslant n_\sigma\leqslant 1$.

In this language, the Radin-Schulman result is easily understood. Any path in a graph may be decomposed into simple cycles [10] (SCs), where a SC is a closed path not visiting any node more than once. If $G_r^{(k)}$ has a unique SC with lower energy per spin than any other, then the nondegenerate periodic ground state of H is generated by repetition of that SC; if there are two or more lowest-weight SCs, then there is always a periodic ground state generated by repeating one of them. In either case, the period of the periodic ground state is at most the number of nodes in $G_r^{(k)}$, which is k^r.

That these SCs are true ground states, in our restricted sense of being stable to perturbations in the Hamiltonian, is readily understood using the idea of the correlation polytope [7,8] $P_r^{(k)}$. The spin correlations are defined by

$$s_\alpha=\langle \sigma_i^{p_0}\sigma_{i+1}^{p_1}\cdots\sigma_{i+r}^{p_r}\rangle, \tag{2}$$

where α denotes the sequence of integers $(p_0,p_1,\ldots,p_r)$; there are $d=(k-1)k^r$ independent spin correlations, given by the values $p_i=0,1,\ldots,k-1$ with $p_0\neq 0$. To any configuration of the chain corresponds a d-dimensional vector $\mathbf{s}$ of correlations, and any Hamiltonian density can be written as a linear combination, $\mathcal{H}=-\Sigma J_\alpha s_\alpha=-\mathbf{J}\cdot\mathbf{s}$, where the J_α are the d independent coupling parameters. However, the mapping from configuration to correlation vector is not one-to-one, and not all correlation vectors represent feasible configurations. Specifically, the correlations and the arc densities are linearly related (Sec. IV), and the constraints $0\leqslant n_\sigma\leqslant 1$ on arc densities translate to inequalities on the correlation vector. They constrain $\mathbf{s}$ to lie inside a convex polytope, and this is the correlation polytope $P_r^{(k)}$.

Because the Hamiltonian is a linear function of the correlations, the ground states that are robust to small changes in couplings J_α are precisely the vertices of $P_r^{(k)}$. By a simple argument [7,8] the vertices can be shown to be in one-to-one correspondence with the SCs of $G_r^{(k)}$, and we arrive at the result that the ground states are ''almost always'' periodic. One can enumerate all possible ground states by finding all SCs of the graph.

The argument just sketched does not apply when a symmetry X is imposed, forcing symmetry-related arc weights to be equal. If the lowest-weight SC is not symmetry invariant, there must be a pair of degenerate lowest-weight SCs. If these do not share a node, there exist two symmetry-broken periodic ground-states. If they share one or more nodes, the domain wall energy between them is zero, so that there are infinitely many degenerate ground state configurations, most of which are mixtures with a nonzero density of domain walls. The latter case is the D-pair phase, so called since it comes from a pair of symmetry-broken configurations, and is characterized by degeneracy (infinitely many ground states, yielding a nonzero entropy density) and disorder (almost all the ground states have no long-range order).

A simple example [8] illustrating the idea of a D pair is the $k=3$, $r=1$ model

$$\mathcal{H}=-\langle\sigma^2\rangle+\langle\sigma_i^2\sigma_{i+1}^2\rangle, \tag{3}$$

where the spins σ_i can take the values 0 and ± 1 and the angular brackets denote an average over the chain. $\mathcal{H}$ is invariant under spin inversion (S) symmetry, $\sigma\rightarrow-\sigma$. It is useful to transform to the variables $\tau=2\sigma^2-1$, which take the values ± 1. The Hamiltonian becomes, apart from irrelevant constants, $\mathcal{H}=\langle\tau_i\tau_{i+1}\rangle$, the Ising antiferromagnet. Its antiferromagnetic ground state, when transformed back to σ variables, is (. . . $\pm 0 \pm 0$ . . .), where each $\pm$ spin can take any value independent of all the others.

The degeneracy and disorder in the ground state appears in this example as a trivial consequence of the double-valued transformation between τ and σ. The reader should not be misled by this apparent triviality. The point in $\mathcal{H}$ space represented by Eq. (3) may indeed be mapped to τ variables in such a way that the degeneracy and disorder vanish. However, this point is surrounded by a finite volume (and hence an uncountable number) of other Hamiltonians, all of which have the same degenerate and disordered ground states—yet none of these other points may be mapped to τ variables.

Specifically, we can add to the $\mathcal{H}$ in Eq. (3) the term $\langle\sigma_i\sigma_{i+1}\rangle$ with a small coefficient. This term (i) conforms to our assumptions that $r=1$ and that $\mathcal{H}$ obeys S symmetry; (ii) spoils the possibility of a mapping to τ variables; (iii) does not split the degeneracy of the state (. . . $0\pm 0\pm 0$ . . .) of Eq. (3); and (iv) leaves the latter state as the ground state. It is precisely this robustness to variations in $\mathcal{H}$ that both characterizes a D pair, and shows that the ground-state degeneracy is not trivial. [For a specific D-pair $\mathcal{H}$ that is not ''trivializable'' by a many-to-one mapping, see Eq. (7) below.]

III. CHARACTERIZING THE *D*-PAIR REGION

To study D-pairs for general k and r, CW introduced the concept of the reduced graph ${}^X G_r^{(k)}$. Not all symmetry-related pairs of SCs of $G_r^{(k)}$ correspond to possible ground states in the presence of symmetry, because the equality of symmetry-related arc weights can imply the existence of a third SC with lower energy than the original pair. We refer to this situation as decomposition of a SC pair. The definitions of the symmetry-reduced graph ${}^X G_r^{(k)}$ and its SCs are tailored to take care of decomposing SCs, in such a way that the possible ground states are in one-to-one correspondence with SCs of ${}^X G_r^{(k)}$. For S symmetry, the reduced graph [Fig. 1(b)] is constructed by identifying each node or arc with its inverse, and SCs are defined as usual as paths that do not self-intersect. For I symmetry, the definition of the reduced graph and its SCs is more involved; we refer the reader to CW for the technical details, including the classification of SCs into four topological types.

The reduced graph ${}^X G_r^{(k)}$ allows the enumeration of the ground-state spin configurations for all D-pair phases with a given k and r. Here, we address the question of the region in the phase diagram in which a given D-pair phase is stable. By the phase diagram, we mean the $d^{(X)}$-dimensional space (reduced from d dimensions by the constraints arising from symmetry) of the coupling parameters J_α.

First, let us discuss the problem unconstrained by symmetry. We ask, what is the region W of $\mathbf{J}$ space in which a given configuration (i.e., SC) ω is the ground state? In principle, it is a region bounded by hyperplanes corresponding to the inequalities $\mathcal{H}(\omega)<\mathcal{H}(\omega')$, where ω' ranges over all other SCs. However, in general some of these inequalities are redundant. We wish to determine the minimal set of inequalities needed to specify W fully. The following two lemmas provide a solution to this problem.

Lemma 1. Suppose the SC ω corresponds to a vertex $\mathbf{v}$ of the correlation polytope. The region W of the phase diagram in which ω is a ground state is specified by the inequalities $\mathbf{J}\cdot(\mathbf{v}-\mathbf{v}')>0$, where $\mathbf{v}'$ ranges over the vertices neighboring $\mathbf{v}$, i.e., those vertices connected in $P_r^{(k)}$ to $\mathbf{v}$ by a one-dimensional edge. Furthermore, this set of inequalities is minimal in the sense that if any one of them is omitted the resulting region is strictly larger than W.

Proof: Let $\{\mathbf{v}_1,\mathbf{v}_2, \ldots ,\mathbf{v}_q\}$ be the vertices of $P_r^{(k)}$ with $\mathbf{v}_1=\mathbf{v}$, and suppose $\{\mathbf{v}_2,\mathbf{v}_3, \ldots ,\mathbf{v}_p\}$ are the neighbors of $\mathbf{v}_1$. Then W is the set of $\mathbf{J}$ such that $\mathbf{J}\cdot(\mathbf{v}_i-\mathbf{v}_1)<0$ for $2\leqslant i\leqslant q$, and we define W' to be the set of $\mathbf{J}$ such that $\mathbf{J}\cdot(\mathbf{v}_i-\mathbf{v}_1)<0$ for $2\leqslant i\leqslant p$. Since $W\subset W'$, to prove $W=W'$ we must show $W'\subset W$.

It follows from the convexity of $P_r^{(k)}$ that the set of vectors $\mathbf{v}_i-\mathbf{v}_1$, $2\leqslant i\leqslant p$, from $\mathbf{v}_1$ to its neighbors spans the full d-dimensional space. In fact, for $j>p$,

$$\mathbf{v}_j-\mathbf{v}_1=\sum_{i=2}^{p}\alpha_i(\mathbf{v}_i-\mathbf{v}_1), \tag{4}$$

for some $\alpha_i\geqslant 0$, with at least two $\alpha_i\neq 0$ [11]. If $\mathbf{J}\in W'$, taking its dot product with both sides of Eq. (4) yields $\mathbf{J}\cdot(\mathbf{v}_j-\mathbf{v}_1)<0$, and hence $\mathbf{J}\in W$, as required.

Define W'' as for W' but omitting one neighbor, say $\mathbf{v}_2$. Since $\mathbf{v}_2$ is a neighbor of $\mathbf{v}_1$ and since $P_r^{(k)}$ is convex, there exists a hyperplane of dimension $d-1$ intersecting $P_r^{(k)}$ only in the edge joining $\mathbf{v}_1$ and $\mathbf{v}_2$. Let $\mathbf{J}$ be a perpendicular vector to this plane from the origin. The sign of $\mathbf{J}$ can be chosen so that $\mathbf{J}\cdot(\mathbf{v}_i-\mathbf{v}_1)<0$ for $i>2$, and thus $J\in W''$, while $\mathbf{J}\cdot(\mathbf{v}_2-\mathbf{v}_1)=0$ implies $\mathbf{J}\notin W$.

Lemma 2. Two vertices in $P_r^{(k)}$ are neighbors if and only if the corresponding SCs of $G_r^{(k)}$ have zero or one contacts, where a contact is a consecutive sequence of one or more shared nodes.

Proof: The vector of arc densities, $\mathbf{n}$, has dimension equal to the number of arcs, but the flow constraints (Sec. II) constrain it to lie in a d-dimensional subspace, which we denote by P'. It is the image of $P_r^{(k)}$ under a nonsingular linear transformation M from $\mathbf{s}$ to $\mathbf{n}$ (see Sec. IV for explicit relations). It follows that neighboring vertices of $P_r^{(k)}$ correspond to neighboring vertices of P'. Two vertices $\mathbf{v}_1$ and $\mathbf{v}_2$ are neighbors if and only if any point $\lambda_1\mathbf{v}_1+\lambda_2\mathbf{v}_2$ (with $\lambda_1+\lambda_2=1$) on the line segment joining them cannot be written as a weighted average of vertices in any other way. Suppose two SCs have two contacts, as illustrated schematically in Fig. 2. Recognizing that the four arc sequences define *four*

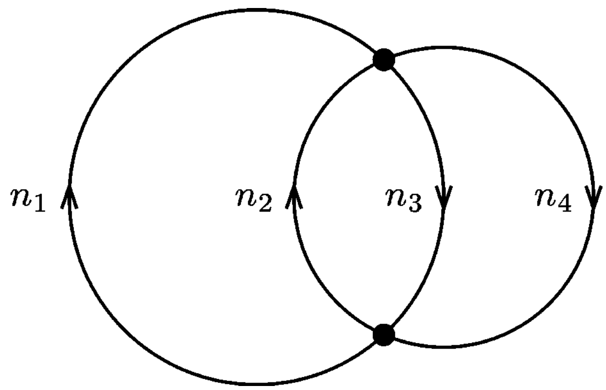

FIG. 2. Schematic picture of simple cycles in $G_r^{(k)}$ having two contacts. The two circles represent the cycles, made up of arc sequences labeled with weights n_1 to n_4, and the large dots are the contacts, which may consist of more than one node.

distinct SCs, we can consider a general convex combination including coefficients λ_3 for the inner cycle (arcs 2 and 3) and λ_4 for the outer cycle (arcs 1 and 4). A point on the line segment joining the corresponding vertices in P' has densities $n_1=n_3=\lambda$ and $n_2=n_4=1-\lambda$. Clearly, there are many convex combinations of vertices yielding the same densities; for example, if $\lambda<1/2$ we can take $\lambda_1=0$, $\lambda_2=1-2\lambda$ and $\lambda_3=\lambda_4=\lambda$. Hence the two SCs correspond to vertices that are not neighbors. Conversely, if the SCs have fewer than two contacts there is only one way to express points in density space on the segment joining them as a convex combination of SCs, and so they correspond to neighboring vertices.

We remark that the reasoning in lemma 2 is very similar to that leading to decomposition of pairs of SCs (except that in lemma 2 the SCs need not be related by symmetry). This has a simple geometrical interpretation. A symmetry imposes linear constraints on the coupling parameters J_α, which means that the relevant space of correlations is a reduced polytope ${}^XP_r^{(k)}$ obtained by symmetry projection of $P_r^{(k)}$. When symmetry-related pairs of vertices of $P_r^{(k)}$ are projected, the ones that become vertices of ${}^XP_r^{(k)}$ are those that are connected by an edge. Indeed, the CW definition of SCs of ${}^XG_r^{(k)}$ (for $X=S$ or I) is constructed so as to include all cycles in $G_r^{(k)}$ that have at most one contact with their symmetry partners. There is, however, one category of nondecomposing SC pairs that does not correspond to neighboring vertices. It has the form of Fig. 2 in the case that symmetry forces the weights to satisfy $w_1=w_2$ and $w_3=w_4$. This situation occurs with I symmetry for a type four SC, when the two contacts are symmetry inverses of each other. Because of the weight constraints all four cycles in the diagram have equal energy, and the original pair does not decompose. It corresponds to two non-neighboring vertices of a quadrilateral face of $P_r^{(k)}$, such that all four vertices of the face map to the same vertex of ${}^IP_r^{(k)}$ under the symmetry.

Lemmas 1 and 2 show how to determine the region in coupling space corresponding to a given ground-state configuration; in fact, they provide an algorithm for doing this. From lemma 1, only neighboring vertices need be considered. Lemma 2 translates the concept of neighboring vertices into properties of graph cycles. In terms of spin configurations, a contact between SCs means a common string of r or more spins.

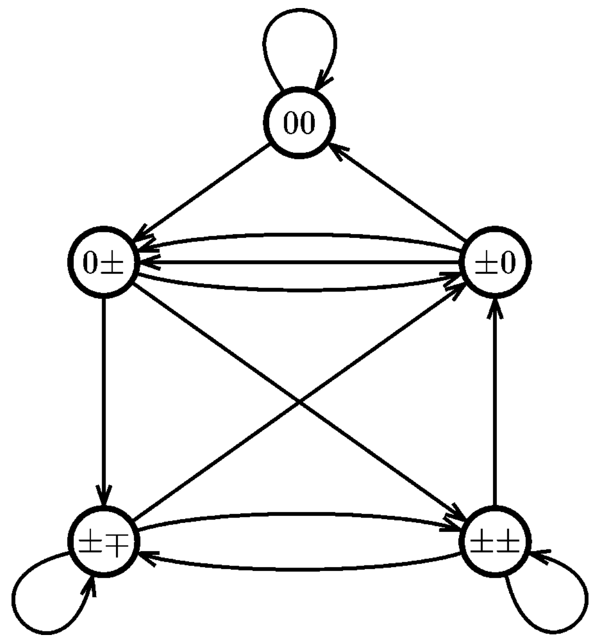

FIG. 3. The reduced graph ${}^SG_2^{(3)}$.

Let us now consider the analogous problem in the presence of a symmetry X. Since Lemma 1 relies only on the Hamiltonian density being a scalar product, it applies directly to the symmetry-constrained problem, i.e., the inequalities defining the stable region W come from neighboring vertices of the reduced (projected) correlation polytope ${}^XP_r^{(k)}$. Lemma 2 also goes through unchanged in the case of S symmetry, since the definition of SCs for ${}^SG_r^{(k)}$ is the same as that for $G_r^{(k)}$. However, lemma 2 does not apply when the symmetry is I.

As in the proof of lemma 2, it is clear that a pair of SCs in ${}^IG_r^{(k)}$ represent neighboring vertices in ${}^IP_r^{(k)}$ if and only if there do not exist two or more new SCs of ${}^IG_r^{(k)}$ using only arcs from the original pair. Because SCs for I symmetry may, when unfolded into $G_r^{(k)}$, represent pairs of intersecting cycles, there is more freedom to form these new SCs than in the absence of symmetry. We find that when the intersection does not contain a symmetric node, then one contact between the original SCs may be enough to imply new SCs. Specifically, we find the following:

Lemma 2′. For I symmetry, two SCs of ${}^IG_r^{(k)}$ correspond to neighboring vertices if and only if one of the following conditions is satisfied: (i) they have no contacts; (ii) they have one contact and one of them is of type one (i.e., unfolds to nonintersecting cycles); (iii) they have one contact that includes a symmetric node. (In the last case, both SCs must be type two or three.)

Let us illustrate our results with the example of $k=3$ and $r=2$ for both S and I symmetries. As in Sec. II we shall take the allowed spin values to be $\sigma=0$ and ±1.

Figure 3 shows the graph ${}^SG_2^{(3)}$. It has 14 arcs, and 5 nodes, each of which implies a flow constraint, leaving 9 independent arc densities, i.e., $d^{(S)}=9$. The 9 symmetry-invariant correlations are $s_1=\langle\sigma^2\rangle$, $s_2=\langle\sigma_i\sigma_{i+1}\rangle$, $s_3=\langle\sigma_i\sigma_{i+2}\rangle$, $s_4=\langle\sigma_i^2\sigma_{i+1}^2\rangle$, $s_5=\langle\sigma_i^2\sigma_{i+2}^2\rangle$, plus four cor-

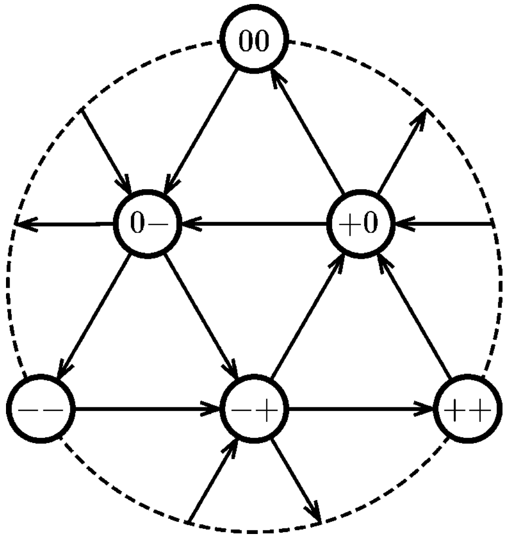

FIG. 4. The reduced graph ${}^{I}G_2^{(3)}$.

relations involving three spins; the Hamiltonian density is written in terms of its 9 coupling parameters as $\mathcal{H} = -\Sigma J_\alpha s_\alpha$. The graph has 19 distinct SCs, 5 of which are D-pairs using the invariant node (00). For example, let us consider the D-pair SC $\omega = (00\pm)$. To find its stable region, we need only consider the 10 SCs that represent neighbors of ω, according to lemma 2. One neighboring SC is the ferromagnetic state (00); comparing its energy to that of ω yields the condition $J_1 > 0$, so we may set $J_1 = 1$. For each of the 9 other neighboring SCs one can write down the corresponding inequality on the 8 remaining couplings directly from the graph. We do not list them here; let us merely display a typical solution:

$$\mathcal{H} = -\langle \sigma^2 \rangle + \langle \sigma_i^2 \sigma_{i+1}^2 \rangle + \langle \sigma_i^2 \sigma_{i+2}^2 \rangle. \tag{5}$$

As in the example of Sec. II it is informative to perform the transformation $\tau = 2\sigma^2 - 1$ to Ising spins. The Hamiltonian becomes

$$\mathcal{H} = \langle \tau_i \tau_{i+1} \rangle + \langle \tau_i \tau_{i+2} \rangle + 2\langle \tau \rangle, \tag{6}$$

which represents an Ising model with antiferromagnetic nearest- and next-nearest-neighbor interactions and a magnetic field favoring the $-$ state. It is easy to check that the ground state is $(--+)$, or in σ variables, $(00\pm)$, as required. Thus we have the degeneracy and disorder characteristic of a D pair. Its robustness to perturbations in the Hamiltonian follows from the fact that all 9 correlations take identical values on every degenerate configuration; i.e., no perturbation made up of s_1 to s_9 can split the degeneracy.

The corresponding reduced graph for I symmetry is shown in Fig. 4. For ease in drawing we have distorted the symmetry line $\mathcal{I}$ into a circle and omitted the ferromagnetic arcs joining each I-invariant node to $\mathcal{I}$. This graph has 32 distinct SCs, most of which are of type three, unfolding to invariant cycles in $G_2^{(3)}$. There are three (type two) D pairs, of which we shall consider the example $(00-+)/(00+-)$. It has 15 neighbors according to lemma $2'$, namely, the ferromagnetic SCs,, the type one SC $(0+-)/(0-+)$, and the 10 type three SCs which use the symmetric node (00). Thus there are 15 inequalities constraining the 14 distinct I-invariant correlations. Again, we do not list them here, but simply display a particular solution, which happens to involve only S-invariant pairwise interactions:

$$\mathcal{H} = \langle \sigma_i \sigma_{i+1} \rangle + \langle \sigma_i^2 \sigma_{i+2}^2 \rangle. \tag{7}$$

The ground state is $(\ldots 00\pm\mp 00\pm\mp 00\ldots)$, where the spins in each $(\pm\mp)$ segment may be chosen independently to be $(+-)$ or $(-+)$. Once again, one can check that this degeneracy is not split by any of the 14 possible I-invariant perturbing terms that may be added to the Hamiltonian.

IV. EXPLICIT D-PAIR HAMILTONIAN

The techniques described in the previous section can be used to find the region of stability corresponding to any given D-pair, for S or I symmetry. However, the analysis becomes tedious for large k and r. In this section, we describe a simple construction for finding a single point, $\mathcal{H}^*$, in the stable region.

The constuction is based on the observation that the arc weights, which determine the Hamiltonian, can all be chosen independently, i.e., for any choice of arc weights there exists a corresponding Hamiltonian. (This statement should not be confused with the fact that the arc *densities* are not independent because of the flow constraints, and hence that the map from arc weights to couplings J_α is not one-to-one.) Given a D pair defined by a SC ω of ${}^{X}G_r^{(k)}$, we define $\mathcal{H}^*$ as the Hamiltonian corresponding to the following assignment of arc weights: w_τ is -1 if the arc τ occurs in the unfolding of the D-pair SC into two intersecting cycles in $G_r^{(k)}$, and 0 otherwise. In terms of arc densities, $\mathcal{H}^*$ is

$$\mathcal{H}^* = -\sum_{\tau \in \omega} (n_\tau + n_{\bar{\tau}}), \tag{8}$$

where the overbar denotes symmetry inversion. By construction, the given D-pair phase is the ground state of $\mathcal{H}^*$: since the energy is the average arc weight, any of the D-pair spin configurations has energy -1, while other configurations use some weight 0 arcs and have higher energy.

In Eq. (8), $\mathcal{H}^*$ is written in terms of arc densities. The latter are related to the correlations as follows. If $\tau = (\tau_0, \tau_1, \ldots, \tau_r)$, then

$$n_\tau = \langle \delta_{\sigma_i \tau_0} \delta_{\sigma_{i+1} \tau_1} \cdots \delta_{\sigma_{i+r} \tau_r} \rangle. \tag{9}$$

The Kronecker delta, as a function of a spin variable σ, can be written as a degree $k-1$ polynomial according to

$$\delta_{\sigma\eta} = \prod_{\eta' \neq \eta} (\sigma - \eta')/(\eta - \eta') = \sum_{p=0}^{k-1} \chi_{p\eta} \sigma^p. \tag{10}$$

The product is over all spin values η' not equal to η, and the second equality defines the numbers $\chi_{p\eta}$ as the coefficients in the polynomial expansion of the product. When this is substituted into Eq. (9) the arc densities are given as a linear combination of spin correlations. From Eq. (8), this yields an expression for $\mathcal{H}^*$ in terms of the correlations. As an example, when this procedure is applied to the D-pair (± 0) for $k=3$, $r=1$ with S symmetry, the result is the Hamiltonian (3), discussed in Sec. II.

Let us investigate further the structure of $\mathcal{H}^*$. Its expression in terms of correlations, from substituting Eqs. (10) and (9) into (8), is

$$\mathcal{H}^* = -\sum_{j=1}^{p}\sum_{p_0=0}^{k-1}\sum_{p_1=0}^{k-1}\cdots \times \sum_{p_r=0}^{k-1}\chi_{p_0\tau_j}\chi_{p_1\tau_{j+1}}\cdots\chi_{p_r\tau_{j+r}} \times \langle \sigma_i^{p_0}\sigma_{i+1}^{p_1}\cdots\sigma_{i+r}^{p_r}\rangle + \text{s.i.} \tag{11}$$

Here, τ_j denotes the jth spin (using any arbitrary starting point) of the configuration defined by the SC ω, and p is the period of ω. The second term, not written explicitly, is the symmetry inverse (s.i.) of the first—that is, every $\tau \mapsto \overline{\tau}$. Consider a range l correlation $s_\alpha = \langle \sigma_i^{q_0}\sigma_{i+1}^{q_1}\cdots\sigma_{i+l}^{q_l}\rangle$, where q_0 and q_l are both nonzero. If $l<r$, there are $(r-l+1)$ terms in Eq. (11) contributing to J_α, the coupling parameter multiplying s_α in $\mathcal{H}^*$. We find

$$J_\alpha = \sum_{j=1}^{p}\sum_{m=0}^{r-l}\chi_{0\tau_j}\cdots\chi_{0\tau_{j+m-1}}\chi_{q_0\tau_{j+m}}\cdots\chi_{q_l\tau_{j+m+l}} \times \chi_{0\tau_{j+m+l+1}}\cdots\chi_{0\tau_{j+r}} + \text{s.i.} \tag{12}$$

The structure of this expression is seen most clearly if we consider initially the case of Ising spins, $k=2$. Taking the allowed spin values to be $\sigma=\pm 1$, we have $\chi_{0\eta}=1/2$ and $\chi_{1\eta}=\eta/2$, and we arrive at the result

$$J_\alpha = 2^{-(r+1)}(r-l+1)\sum_{j=1}^{p}\tau_j^{q_0}\tau_{j+1}^{q_1}\cdots\tau_{j+l}^{q_l} + \text{s.i.} \tag{13}$$

This result is quite significant. It says that the value of J_α is, apart from a constant $2^{-(r+1)}$ that we shall ignore, equal to $(r-l+1)[t_\alpha+\text{s.i.}]$, where t_α is the correlation s_α evaluated in the spin configuration $\{\tau_i\}$ of the D pair.

Since a correlation for Ising spins has magnitude at most 1, this implies the bound $|J_\alpha| \leqslant (r-l+1)$. Further, we note that t_α is expected not to be strongly dependent on the range l of the coupling J_α. Roughly speaking, spin configurations that have long-range correlations tend also to be correlated at short range. This idea is borne out by explicit computations; for instance, for the I symmetry $r=5$ Ising D pair $(+----++-)$, there are 23 symmetric correlations, each of which takes one of the values $-1/7$ or 3/7, with no systematic dependence on l. Thus, the dominant contribution to J_α comes from the factor $(r-l+1)$. As a function of distance, this represents a linear decrease to zero at the cutoff range $l=r+1$.

For $k>2$, the situation is similar. Of course, the values of the couplings depend on the choice of the set of allowed spin values, which has been left arbitrary so far. However, for any k there exists a choice with the property that $\chi_{0\eta}$ is independent of η, namely, letting $\{\sigma\}$ be the complex kth roots of unity. For this choice, the sum (12) simplifies as it did for Ising spins, yielding (apart from a constant) $J_\alpha=(r-l+1)[t_\alpha+\text{s.i.}]$. Under the assumption that the correlations t_α depend weakly on l, we find again that the dominant distance dependence of J_α is a linear falloff to zero beyond the cutoff range.

V. DISCUSSION

The existence of D-pair phases is interesting from a theoretical point of view. However, we are not aware of any obvious candidate material for their realization in nature. We note that there is an entire class of materials, namely, layered solids or polytypes, that is well modeled by effective Hamiltonians such as those studied here. This class of materials is, however, quite large; and the few effective Hamiltonians that are known from this class do not show promise of having a D-pair phase as the ground state. (See the discussion and references in Ref. [12].)

Thus, there are significant obstacles to finding D pairs in practice. However, the results of Sec. IV of this paper remove one potential obstacle: the possibility that the only Hamiltonians exhibiting D-pair phases are pathological in the dependence of their coupling parameters on distance. We would like the couplings to decrease smoothly to zero at the cutoff range, otherwise it would seem unphysical to impose a rigid cutoff beyond which there are no interactions. We have constructed an explicit Hamiltonian for arbitrary k and r, which has D-pair ground states. Encouragingly, its couplings are very well behaved: as a function of distance, they fall linearly to zero at the cutoff.

Remaining obstacles concern the robustness of D-pair behavior. Although D-pairs are not destroyed by symmetric perturbations of sufficiently short range or by nonzero temperature, they are in general destroyed by including interactions beyond the cutoff. They are also destroyed by deviations from perfect symmetry caused, for example, by external fields—which may or may not be strictly zero, depending on the symmetry in question, and on the physical identity of the ''spins.'' However, even when the degeneracy is broken in such ways, behavior characteristic of D pairs may be observable at a suitable energy scale. If the perturbations breaking the D-pair symmetry are small, they are not manifest except at very small temperatures. At low but nonzero temperatures, one would still expect to observe disordered states and nonzero entropy density. In that case, the techniques of Sec. III of this paper apply directly to the problem of characterizing the D-pair region. (Possible experimental signatures of D-pairs have been investigated by Yi and Canright [12].)

Another potential obstacle is the limitation to problems involving classical, discrete units. However, such models are likely to be good approximations for certain problems, such as stacking polytypes of crystals (see CW and references therein) where the ''spin'' represents the discrete set of possible configurations of a single lattice plane. Another limitation is the restriction to one-dimensional models. The question of whether similar behavior is possible in higher dimensions is unexplored, although certain frustrated two-dimensional models are known to have degenerate ground states of large periodicity [13]. Finally, although we have shown that D-pair phases are possible with Hamiltonians that are not obviously unphysical, there may be more subtle physical reasons—arising, say, from quantum-mechanical considerations—which may argue against effective classical Hamiltonians having D pairs as ground states. For example, effective classical Hamiltonians representing the binding energy of mobile electrons in an ionic background tend to favor periodic ionic arrangements [14]. We leave these questions for future work.

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