Transmission of Order in Some Unusual Dilute Systems

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As a system is diluted, the critical temperature T_c may fall to zero at a concentration x_c greater than the percolation concentration p_c, because mere connectivity does not guarantee the transmission of order even at $T=0$. Detailed results, including bounds on x_c, are presented for the three-state Potts antiferromagnet on a triangular lattice and for quadrupolar models of $(o\text{-H}_2)_x(p\text{-H}_2)_{1-x}$ mixtures on fcc and triangular lattices.

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It has been generally believed that when magnets are quench diluted the onset of long-range order (LRO) at $T=0$ occurs at a concentration x_c equal to p_c, the percolation threshold, independent of the type of interaction.[1] Even the short-range Ising $\pm J$ spin-glass now seems to conform.[2] We describe exceptions, however, in which x_c is significantly higher than p_c for nonlocal geometric reasons. Whereas conventional percolation depends on a single connected path through the lattice, certain systems require multiple neighbors or multiple paths through the lattice. Single paths may transmit partial order, and a particular site may be ordered by the receipt of partial order from two or more widely separated paths. Because of this nonlocal contribution to ordering, x_c cannot be computed directly by use of ordinary percolation algorithms.

We exemplify systems with $x_c > p_c$ by the nearest-neighbor three-state Potts antiferromagnet on a triangular lattice[3] (3-PAFT), and by models of hydrogen molecules on fcc and triangular lattices. The work was motivated by the experimental observation[4] that x_c is approximately equal to p-H$_2$-diluted o-H$_2$ and o-D$_2$-diluted p-D$_2$, with x_c (≈ 0.53) much larger than p_c (0.195 for fcc[5]). The similarity of x_c values in H$_2$ and D$_2$ suggests that quantum effects (which are much smaller in D$_2$) are not responsible for the discrepancy between x_c and p_c, but rather that their common geometry is crucial.

Order transmission is trivial in dilute ferromagnets (F) and in dilute isotropic antiferromagnets (AF) with two possible spin states (Ising). These always have $x_c = p_c$, because each occupied site requires only one ordered neighbor to tell it which state to choose—the same for F, the opposite for AF. A second occupied neighbor is required if the site is to transmit its order to another; otherwise, it can play no role in global ordering. For order to be passed across a sample we require an infinite cluster of sites with two occupied neighbors, which occurs by definition at p_c. Thus $x_c = p_c$.

The site-diluted 3-PAFT appears to be the simplest nontrivial system having $1 > x_c > p_c$. The model is defined by the Hamiltonian

$$\mathcal{H} = J \sum_{(ij)} \varepsilon_i \varepsilon_j \delta(\sigma_i, \sigma_j), \qquad (1)$$

where J is a *positive* constant, ε_i is 1 with probability p and 0 otherwise (quenched), σ_i is a three-valued dynamical variable (e.g., $\sigma_i \in \{A,B,C\}$), and the sum is over nearest-neighbor pairs. There are six degenerate ground states in the pure system ($p=1$), as illustrated at the top of Figs. 1(a)–1(f). Among antiferromagnetic q-state Potts models the $q=3$ case is actually very special[6]; for $q \geq 3$ (bipartite lattices) the ground-state entropy is nonzero, and for $q=2$ (bipartite) the ground states are frustrated. In the 3-PAFT alone we can concentrate on the transmission questions, since the ordering in the undiluted system is relatively simple. For the *bond*-diluted 3-PAFT Ono[7] has suggested that $x_c > p_c$ from the extrapolation of finite-T results. We consider the *site*-diluted case, which is more amenable to analysis and closer to experiment, and demonstrate without extrapolation that $x_c > p_c$ even at $T=0$.[8]

We discuss the transmission of order at $T=0$ in the 3-PAFT, from top to bottom in Figs. 1(a)–1(f). The upper part is presumed ordered in one of the six ground states as shown, whereas the lower part is ordered only in 1(a) and 1(f). In the other cases the star and inverted triangle symbols represent partial order with two choices (such as A or B) and no order (A or B or C), respectively. In Fig. 1(a) every site has at least two different neighbors in the row above, and is thus uniquely determined; order is passed from row 1 to row 10. In Fig. 1(b), while the sites of rows 1–4 are determined, the site in row 5 is only constrained not to be in state B, those in rows 6 and 7 are entirely undetermined, and those in 9 and 10 could be in any of the six ground states. There is no transmission of LRO.

For order to be transmitted across a site-diluted 3-PAFT there must be *at least* an infinite cluster of sites which have *three* occupied neighbors, two to tell them which state to choose and a third to which to pass the information. This defines the $m=3$ bootstrap percolation[9] critical concentration, $p_3 = 0.628 \pm 0.008$,[10] which is considerably above $p_c = 0.5$.[5] For $x \leq p_3$ there can be no LRO at $T=0$, and so we have $x_c \geq p_3 > p_c$.

A slight improvement to this lower bound for x_c can be made by consideration of Fig. 1(c). Here LRO cannot be transmitted even though each site has three occu-

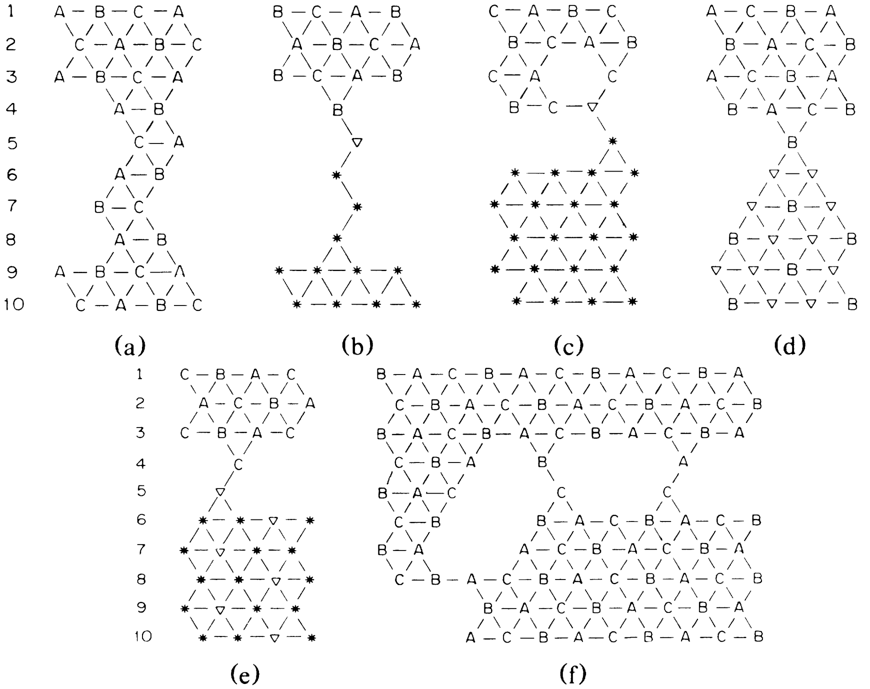

FIG. 1. Illustration of the propagation of order in a diluted three-state Potts antiferromagnet on a triangular lattice at $T=0$. The three possible Potts states are A, B, C. Unoccupied sites are not shown. Sites that have two possibilities, (e.g., A or B) are shown as inverted triangles. Sites that are completely undetermined relative to the top row (but not necessarily relative to their neighbors) are shown as stars. Adjacent occupied sites are joined by solid lines for ease of reading.

pied neighbors. The rightmost site in row 4 has a choice of two states because the two neighbors give it the same information. Each site requires more than information from two occupied neighbors—it requires that they be on different sublattices. Thus a necessary condition for the passage of LRO is the presence of an infinite cluster of sites that have three neighbors, at least one on each of the other two sublattices. For the 3-PAFT this is equivalent to the requirement that two of the neighbors be neighbors of each other. We have estimated the critical concentration p_3' for this condition from simulations of up to 500 lattices with 30×30 sites, periodic boundary conditions, and finite-size scaling. We find $p_3'=0.635 \pm 0.01$, slightly higher than p_3.

The configurations of Figs. 1(d) and 1(e) are very interesting. While LRO fails to be transmitted to either case we see that *partial order* is transmitted because the lower half of 1(d) is restricted to two of the six ground states and that of 1(e) to a choice of four. Certain combinations of such links can transmit LRO, as in Fig. 1(f), because each transmits partial information. All three links are needed in 1(f), but other cases in which two are enough can be constructed. The determination of the passage or not of LRO in the 3-PAFT clearly requires a knowledge of the long-range connective geometry of the system. The precise determination of x_c cannot therefore employ the usual fast Hoshen-Kopelman percolation algorithm,[11] even with the preselection of sites used to compute p_3 and p_3'.

We have demonstrated that $x_c > p_c$ in the 3-PAFT. We now exclude the possibility that $x_c=1$ by providing an upper bound on x_c. An upper bound is easily obtained via a local algorithm by our looking for the percolation of occupied *triangles* (on the dual lattice). We call a triangle of three occupied mutual neighbors *connected* to another if they share a common edge. Connected triangles clearly transmit order, as in Fig. 1(a), but are not necessary for LRO, as seen in Fig. 1(f). The triangle percolation condition is actually equivalent to explicitly discounting the failing bridges of Figs. 1(d) and 1(e) from the p_3' condition. We obtain a critical concentration for triangle percolation of $p_t=0.782 \pm 0.004$ from simulations of up to 30×30 sites. Together we have bounds $0.635 \pm 0.01 \leq x_c \leq 0.782 \pm 0.004$.

We now consider the quenched site dilution of nearest-neighbor *quadrupoles* in a Pa_3 ground state[12] on the fcc lattice. This is appropriate for molecular-hydrogen mixtures of quadrupolar o-H_2 diluted by inert p-H_2, or quadrupolar p-D_2 diluted by inert o-D_2. We consider only the breakdown of the ordered Pa_3 phase on the fcc lattice, not the phase (possibly glassy) that replaces it for $x < x_c$. Two isolated quadrupoles have lowest energy when mutually perpendicular, but on the fcc lattice they are forced by a form of frustration into the compromise four-sublattice Pa_3 structure. For the present purpose we will represent the diluted system by a four-state model, in which each quadrupole is specified fully by an axis direction **n** lying along one of the four $\langle 111\rangle$ directions, with Hamiltonian

$$\mathcal{H}=\sum_{(ij)}\varepsilon_i\varepsilon_j V(\mathbf{n}_i,\mathbf{n}_j,\mathbf{r}_{ij}). \tag{2}$$

Here $\mathbf{r}_{ij}$ is the vector joining nearest neighbors i and j (e.g., $\mathbf{r}_{ij}=[110]$), and the interaction energy V is given by the full electric quadrupole-quadrupole interaction[12] between ground-state molecules. The pair interaction $V(\mathbf{n}_i,\mathbf{n}_j,\mathbf{r}_{ij})$ is minimized when $\mathbf{n}_i\neq\mathbf{n}_j$ and $(\mathbf{n}_j\cdot\mathbf{r}_{ij})\times(\mathbf{n}_j\cdot\mathbf{r}_{ij})=0$. Nonminimal configurations need not be considered within the four-state model because no frustration remains—all pair interactions can be simultaneously minimized. In isolation, six of the twelve neighbors of a given fixed quadrupole have three alternative states, and six have only two. This four-state model explicitly ignores the *canting* away from the $\langle 111\rangle$ directions that occurs on dilution,[13] as discussed below.

In the four-state model, it is clear that ordinary percolation is insufficient to produce LRO since a single chain of occupied sites [cf. Fig. 1(b)] can certainly not propagate order. In order for a quadrupole to know which of the four orientations to choose it must have *at least* two neighbors on different sublattices. To pass order, a third site is needed and thus p_3 again provides a lower bound for x_c. An *upper bound* on x_c is provided by the $m=7$ bootstrap percolation concentration p_7 because, as is easily shown, a quadrupole surrounded by any seven ordered neighbors is always uniquely ordered. Recent simulations for the fcc lattice[14] provide $p_3=0.30\pm0.02$ and $p_7=0.81\pm0.02$, giving overall $0.30\le x_c\le 0.81$ for the four-state model, compared to $p_c=0.195$.[5] These bounds are based on fast local algorithms; sharper estimates for x_c could be obtained by a simulation incorporating nonlocality.

The real hydrogen system differs from the four-state model in that hydrogen molecules in diluted surroundings will not in general adopt one of our four states.[13] Indeed, the four $\langle 111\rangle$ directions in the Pa_3 structure only occur as a compromise in the presence of frustration, which is relieved by dilution.[15] The resulting canting of the quadrupoles may reduce but cannot increase the transmission of order, so that in all we have

$$x_c(\text{hydrogen})\ge x_c(\text{four-state model})\ge p_3>p_c. \tag{3}$$

Our bound for hydrogen is thus $x_c\ge p_c=0.30$, consistent with the experimental result[4] $x_c\approx0.53$ for both H_2 and D_2. The value of x_c can also be estimated by other nongeometrical methods, taking a $T\to0$ limit; for the fcc lattice[16] the Bethe-Peierls approximation suggests $x_c\approx\frac{1}{6}$ and a Kirkwood restricted-trace approach gave $x_c\approx0.5$. Such estimates do not, however, have controlled errors.

Our result clearly shows the importance of geometry in the orientational ordering of hydrogen. Although our results are obtained for $T=0$, we expect that geometry will be important for $T>0$ too. The experimental $x_c(T)$ approaches a well-defined limit as $T\to0$, with $dT/dx_c\to\infty$. *Partial ordering* may also occur for $1>x>x_c$ in hydrogen, and probably accounts for the observation in NMR experiments[17,18] of an orientational LRO parameter approaching less than its maximal value as $T\to0$.

We can apply similar reasoning to o-H_2-p-H_2 mixtures on a two-dimensional triangular lattice, appropriate to adsorption on graphite.[19,20] A four-state "pinwheel" ground state forms in the pure system. However, a four-state model corresponding to Eq. (2) is not strictly applicable because of the inequivalence of the four orientations; in some cases the electric quadrupole-quadrupole interaction could allow a *single* neighbor to order a quadrupole correctly given the four-state restriction. A more detailed analysis allowing for canting[21] suggests that at least two neighbors are needed to order a molecule in the unrestricted case, and so, allowing again for the onward transmission of order, we expect that $x_c\ge p_3=0.628$ on the triangular lattice.[10] This is consistent with the experimental results,[20] which extrapolate to $x_c\approx0.7\pm0.1$ as $T\to0$.

Shnidman and Mukamel[15] have considered another mechanism for $x_c>p_c$ in diluted *frustrated* systems. Dilution tends to relieve frustration and reduces order because some sites reorient in the absence of certain neighbors. This effect may give a strict inequality x_c(hydrogen) $>x_c$(four-state model); cf. Eq. (3). Our mechanism can occur in both frustrated and unfrustrated systems, but only if there are more than two possible states at each site (i.e., not Ising). Both mechanisms rely fundamentally on the existence in the pure system of multiple (but not necessarily conflicting) ordering information arriving at a site through the different bonds. In the diluted system the lack of some such information at a given site can lead to (a) lack of order, (b) partial order, (c) incorrect order, or (d) canting. We have emphasized (a) and (b), whereas Shnidman and Mukamel consider (c). Case (d) may be considered a special case of (c) where the local orientation falls outside the normal manifold found in the ground state. Cases (c) and (d) only occur in frustrated systems, but, as we have shown, $x_c>p_c$ can occur in cases (a) and (b) too, and is thus not a special feature of frustration.

The approach considered here is widely applicable. The demonstration that geometry rather than quantum effects is responsible for some experimentally observed $x_c>p_c$ cases suggests a further look at other dilute systems with complex ground states, such as metamagnets and plastic crystals. Partially ordered clusters, and perhaps a partially ordered phase, may well occur in other diluted multistate systems, including short-range Potts spin-glasses.[22] The surprising result that the passage or not of LRO depends on the overall cluster geometry even with nearest-neighbor interactions suggests a connection with rigidity percolation.[23]

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