

Some developments in the theory of modulated order.  
 II. Deformable-lattice models and the axial next-nearest-neighbor Ising model  
 as a random magnet

Tony DeSimone\* and Richard M. Stratt

*Department of Chemistry, Brown University, Providence, Rhode Island 02912*

Jan Tobochnik

*Department of Physics, Clark University, Worcester, Massachusetts 01610*

(Received 13 February 1985)

This paper presents a new class of models capable of producing modulated order with solely nearest-neighbor forces. These *deformable-lattice models* create modulated phases out of the interaction between spin and elastic degrees of freedom through a polarization, or feedback, mechanism—as opposed to the purely spin or purely elastic models that employ either competing force or competing periodicity mechanisms. We show that one of the deformable-lattice models, in particular, can be formally reduced to the axial-next-nearest-neighbor Ising (ANNNI) model. This observation turns out to imply, first, that the ANNNI model can be regarded as an ordinary Ising model with a distribution of coupling constants (a random magnet), and second, that other spin models might be profitably thought of not as Hamiltonians, but as potentials of mean force resulting from integrating out elastic degrees of freedom. The possible implications are considered for both the range and nature of the interaction between chemisorbed species as well as that between intercalates in graphite.

### I. INTRODUCTION

In this paper we will continue our study of the general features of modulated order in solids. However, rather than focusing on a particular model displaying modulated order, as we did in the companion paper,<sup>1</sup> we will instead try to consider just what characteristics are essential to a Hamiltonian which can give thermally stable patterns.<sup>2,3</sup> The most commonly cited of such Hamiltonians, the axial next-nearest-neighbor Ising (ANNNI) one,<sup>4</sup> is actually reasonably narrowly defined: it postulates a unique direction in space, interactions which are longer ranged than nearest neighbor and which compete with each other, and it has just one kind of degree of freedom. Clearly not all of these properties can be equally vital.

The requirements on the range of interaction are of particular current interest in view of the nature of staging in graphite intercalation compounds.<sup>5</sup> These compounds are formed when electron donors (such as alkali metals) or Lewis acids (such as Br<sub>2</sub> and SbF<sub>5</sub>) are allowed to migrate between the layers of graphite. When they do so, however, the resulting solids are stable only when the intercalating species form a pattern of filled and empty layers known as a "stage." A stage-*n* compound, for example, is one in which there are *n* graphitic layers between successive intercalate layers. Since there are experimental instances<sup>6</sup> of values of *n* as high as 13, there exist patterns with periodicities as large as 45 Å. One could thus ask whether this observation implies that the interactions themselves are of this range.

The current models<sup>7,8</sup> for graphite intercalation staging do indeed postulate very-long-range interactions. In fact,

the periodicities one gets out of such models are no longer than the range of the longest interaction. While this kind of purely energetic model for modulated order may be appropriate for graphite, it certainly will not serve as a prototype for the field. Even the ANNNI model can produce large periodicities with no more than next-nearest-neighbor forces.<sup>9</sup> Maybe an example of what one might want to know is whether one can do so with only nearest-neighbor forces.

With ordinary spin models, the answer will usually be no. (An exception is the chiral clock model.<sup>10</sup>) However, there is no reason to limit our considerations to models involving just spin degrees of freedom. There have, for example, been numerous models in which *elastic* interactions are explicitly included in the treatment of pattern-forming systems. In particular, both graphite intercalation<sup>8</sup> and the ferroelectric transition in squaric acid<sup>11</sup> have been studied with phenomenological elastic terms added to the spin Hamiltonians. Unfortunately, for our purposes these cases are not especially germane because the elastic effects are solely a quantitative modification of the modulation already caused by the underlying spin-spin interactions.

Perhaps more relevant are models involving *only* elastic degrees of freedom. The most celebrated of these, the Frenkel-Kontorova model,<sup>12</sup> generates modulated order from competing periodicities. It has been shown that this model can be translated into a sine-Gordon equation,<sup>13</sup> making it possible to think in terms of the pinning and depinning of solitonlike domain walls<sup>2</sup> and consequently allowing a treatment of the commensurate incommensurate transition.<sup>14,15</sup> Still, even models of this sort do not exhaust the possibilities for creating nonuniform order.

Conspicuous by their absence are models in which the *interaction* between elastic and spin degrees of freedom is responsible for the modulation.

This state of affairs is really somewhat surprising in view of the numerous ordering phenomena in solid-state physics which have electron-phonon coupling as their central feature. To cite just one example, the coupling of phonons with electronic structure leads to a Peierls<sup>16</sup> distortion in conjugated polymers. Thus polymers with alternating single and multiple bonds, such as polyacetylene,<sup>17</sup> can be thought of as existing in a modulated structure often called a bond-order wave.<sup>18</sup> There is no real counterpart to such phenomena in the literature of classical spin models. This is not to say that there has not been considerable effort devoted to thinking about elastic effects in magnetic systems. Indeed, compressible-lattice models have been studied extensively, both at a macroscopic level<sup>19,20</sup> (starting with Mattis and Schultz) and at a Hamiltonian level<sup>21–24</sup> (beginning with Baker and Essam), but such models do not lead to any kind of modulated order. The closest example of a spin-phonon system which does give at least some ordering besides that of a simple ferromagnet is the compressible-lattice model recently discussed by Chen and Kardar.<sup>25</sup> Here, at least, it is the physics of the interaction between different kinds of degrees of freedom which can rise to a pattern, but even here one obtains nothing more complex than antiferromagnetic ordering.

Mostly out of a desire to discover the possible mechanisms for the creation of thermally stable patterns, in this paper we will be presenting models in which nearest-neighbor spin interactions couple with nearest-neighbor elastic interactions to create modulated order. Section II of the paper will show how these models generate modulated order, not through the usual mechanism of competing forces but rather through polarization effects. Some examples of the kinds of ground states such models can give—including patterns reminiscent of staging and surface superlattices<sup>26</sup>—will also be discussed in this connection. Section III will then illustrate how integrating out the elastic degrees of freedom can give us back various spin models, and in particular, the ANNNI model. In addition, it will be shown how finite-temperature phase diagrams of these spin models can be calculated from mean-field theory. Finally, in Sec. IV the relationship between the models discussed here and a few of those in literature will be examined. Not surprisingly, in view of our companion paper, this comparison will include models of spin glasses.<sup>27</sup>

## II. FORMULATION OF THE DEFORMABLE-LATTICE MODEL: THE GROUND STATE

### A. A one-dimensional example

Suppose we consider the one-dimensional Ising model defined by the Hamiltonian

$$\mathcal{H} = \sum_j (-J\mu_j\mu_{j+1} - H\mu_j),$$

where the  $\mu$  variables ( $= \pm 1$ ) are the Ising spins,  $J$  is the

coupling constant, and  $H$  is the magnetic field. A question one might ask is in what way the ground-state statistical mechanics would be different if the underlying lattice were allowed to move in response to the spins. As we have previously noted, this question has already been asked and answered in considerable detail—at least for certain kinds of spin-lattice couplings.<sup>24</sup> However, we can consider a slight variation on the existing models.

Suppose we also assign a continuous deformation variable  $\phi_j$  to each lattice site  $j$  ( $-\infty < \phi_j < \infty$ ). Presumably, whatever interaction there is between spins  $j$  and  $j+1$  should increase as the spins move closer together and decrease as they separate. Thus, taking the simplest Hamiltonian displaying this property (one in which the effective coupling constant between spins depends linearly on the distance between the spins), we might write

$$\mathcal{H} = \sum_j \{ k\phi_j^2 - J[1 - \alpha(\phi_{j+1} - \phi_j + \Delta)]\mu_j\mu_{j+1} - H\mu_j \}, \quad (2.1)$$

with  $k$  the harmonic spring constant associated with each site,  $\alpha$  the spin-lattice coupling constant ( $0 < \alpha < 1$ ), and  $\Delta$  the lattice spacing.

This model, at first glance, seems somewhat less physical than, say, the Baker-Essam<sup>21</sup> model, in which the harmonic deformation term goes as  $(\phi_{j+1} - \phi_j)^2$  rather than  $\phi_j^2$ . The  $\phi$  variables need not be thought of as simple displacements however. They could represent any sort of elastic variable—the local distortion of graphite sheets in intercalated graphite<sup>28</sup> or the deformation of a surface atom with respect to the bulk, for example. We will not pursue their specific physical interpretation any further here (although we will return later to the relationship between our model and literature models). We might also note that the linear coupling actually permits the effective coupling constant

$$J[(1 - \alpha\Delta) - \alpha(\phi_{j+1} - \phi_j)]$$

to change sign when the deformation becomes large enough. We, similarly, will not comment on what types of interactions would be expected to have this property.<sup>29</sup>

Still, if we do adopt the model as written, it is revealing to determine its ground state. Minimizing the Hamiltonian with respect to the deformation identifies the ground-state deformations as

$$\phi_j = (J\alpha/2k)\mu_j(\mu_{j+1} - \mu_{j-1}) \quad (2.2)$$

so that the obvious candidate, the uniformly ordered ferromagnet with zero deformation ( $\mu_j = 1$ ,  $\phi_j = 0$  for all  $j$ ), qualifies. An alternate possibility though, is to have a modulated spin pattern with two spins up, then two spins down, leading to deformations which are alternately plus, then minus,  $J\alpha/k$ . These two ground states are shown in Fig. 1(a).

The energies of these two phases can easily be calculated from Eq. (2.1). At zero field,

$$E_{\text{ferro}}/Nk = -(J/k)(1 - \alpha),$$

$$E_{\text{mod}}/Nk = -(J/k)^2\alpha^2$$

(where we have chosen units so that  $\Delta = 1$ ). As can be

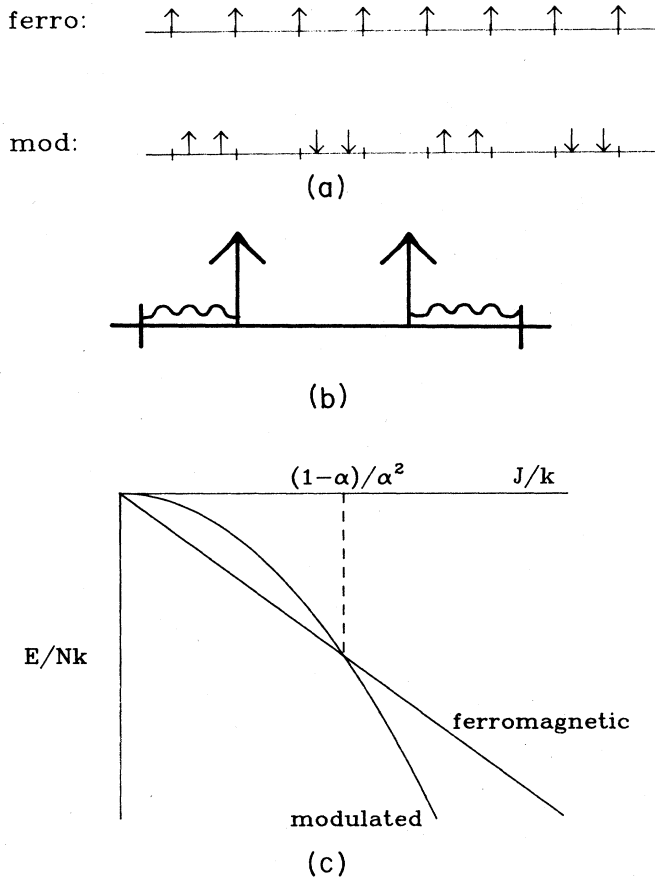


FIG. 1. (a) Two possible ground states of the deformable-lattice model: a uniform ferromagnetic (ferro) pattern and a deformed, modulated (mod) pattern. The spins in the modulated pattern are deformed from their lattice sites (indicated by tic marks), but the unfavorable energy of deformation [symbolized by the springs in (b)] is compensated by the more favorable spin-spin interaction. In (c) the energy per spin of the two phases is plotted vs coupling constant  $J$  (both quantities scaled by the spring constant  $k$ ). The quadratic dependence of the energy of the modulated phase results in a modulated ground state for  $J/k$  larger than  $(1-\alpha)/\alpha^2$ .

verified from Fig. 1(c), at large enough interaction strengths, the quadratic dependence of the modulated phase on  $J/k$  will eventually dominate the linear dependence of the ferromagnetic phase, making the modulated phase the actual ground state. But while any number of functional dependences would be sufficient to overcome a linear term, it is indicative of the fundamental origin of the modulation that the term is quadratic. The quadratic form arises here because not only is the deformation created by the interaction [Eq. (2.2)] but the interaction energy itself is proportional to the deformation [Eq. (2.1)]; i.e., if the deformation  $\sim J$ , then the energy which is  $\sim -J \times (\text{deformation})$  is  $\sim -J^2$ .

The end result is that the mechanism for the creation of modulated order is a *polarization* (or reaction-field) mechanism<sup>30</sup> and not, for example, just competing forces.

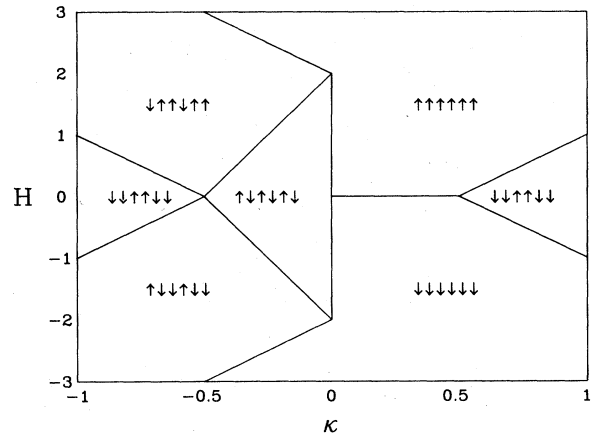


FIG. 2. Ground-state phase diagram of the one-dimensional Ising version of the deformable-lattice model, Eq. (2.1). As the magnitude of the field,  $H$ , is increased, a phase with a net moment becomes the ground state. The dependence on coupling constants is through the parameter  $\kappa$ , defined in Eq. (2.3). As will be discussed in Sec. III, this figure is identical to the ground-state phase diagram of the ANNNI model (Ref. 34).  $H$  is measured in units of  $J(1-\alpha) = J_1$ .

Indeed, the very possibility of deformations is what allows spins to shift their positions so as to lower the energy of previously unfavorable spin-spin interactions, prompting neighboring spins to do the same, and thereby stabilizing both the original spin pattern and the deformation. It should also be clear that this mechanism is not limited to producing just one type of modulation. If one allows both ferromagnetic and antiferromagnetic values of  $J$  and permits a nonzero magnetic field, one produces a zero-temperature phase diagram with a wide variety of phases (Fig. 2).

In particular, defining  $\kappa$  to be

$$\kappa \equiv (J/2k)\alpha^2/(1-\alpha), \quad (2.3)$$

reveals that the point  $\kappa = \frac{1}{2}, H = 0$  is a multiphase point at which an infinite number of phases coexist. The general form of these phases (illustrated in Fig. 3) is that of domains of (at least two) parallel spins, with each domain antiparallel to the previous one. From Eq. (2.2) one knows that the interior of such domains cannot lead to a (pattern-stabilizing) deformation, but at the boundaries the spins can be deformed so as to separate antiparallel spins and lessen the distance between parallel spins. Precisely at the multiphase point, then, the resulting domain walls turn out to have no self-energy. The walls are therefore free to translate up and down the chain (generating an infinite number of degenerate phases in their wake). A

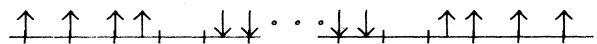


FIG. 3. A possible pattern for one of the degenerate phases at the  $(\kappa = \frac{1}{2}, H = 0)$  multiphase point in Fig. 2, showing the deformations at domain walls. As indicated by Eq. (2.2), finite deformations exist only at sites between unlike spins.

similar analysis would predict analogous degeneracies at  $\kappa = -\frac{1}{2}$  as well as along some of the phase boundaries.

### B. Some generalizations

Even confining ourselves to one dimension, there are a number of obvious, physically motivated generalizations of Eq. (2.1). The easiest of these would be to regard the  $\mu$  variables as more general spin variables  $s$ :

$$\mathcal{H} = \sum_j \{ k\phi_j^2 - J[(1-\alpha) - \alpha(\phi_{j+1} - \phi_j)]s_j s_{j+1} - Hs_j \}. \quad (2.4)$$

In particular, one might want to make  $s$  a lattice-gas variable (0,1) so that two occupied ( $s=1$ ) neighboring sites would be needed to produce a deformation.<sup>31</sup> Such a choice would lead to the phase diagram shown in Fig. 4. As an illustration of how one might interpret this kind of model, consider the graphite example mentioned in Sec. II A. If we were to let  $\phi_j$  correspond to distortions in the spacing of the graphitic layers bordering intercalation-“site”  $j$ , then  $\phi_j$  would be nonzero only if site  $j$  were filled with intercalate ( $s_j=1$ ) and if the two neighboring sites were filled asymmetrically (e.g.,  $s_{j-1}=1, s_{j+1}=0$ ). Alternate realizations of the deformation variables, with correspondingly different choice of physical situations in which deformations occur, could, of course, be implemented in a Hamiltonian with the same general features as Eq. (2.4).

For our immediate purposes, a more useful set of generalizations would be to extend the Hamiltonian to higher dimensions. Clearly, without such an extension the modulated phases have no finite-temperature significance, but there are nonetheless many different ways to effect the generalization. On a square lattice one way, a *symmetric* version, would be to define a deformation vector

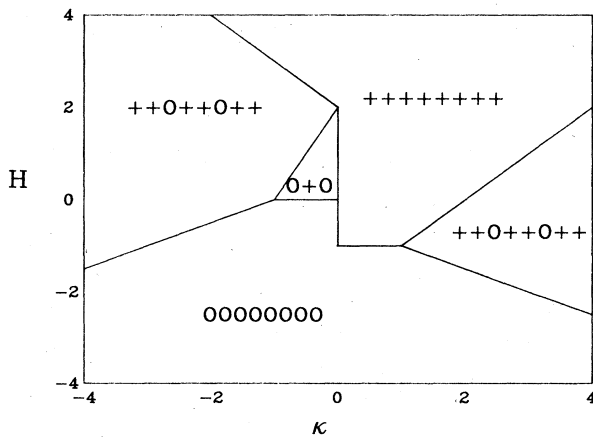


FIG. 4. Ground-state phase diagram of the one-dimensional binary-variable-lattice model, Eq. (2.4). A + indicates an occupied site ( $s=1$ ) and a 0 indicates a vacant site ( $s=0$ ). The axes are labeled as in Fig. 2. The method used in deriving this phase diagram is outlined in the Appendix.

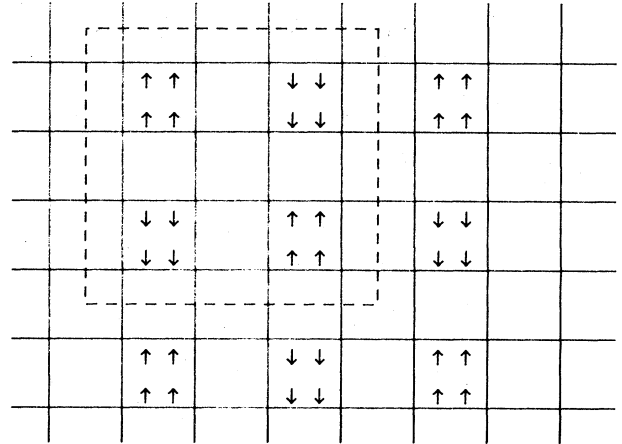


FIG. 5. A ground state of the symmetric two-dimensional version of the deformable-lattice model, Eq. (2.5). The spins are connected by harmonic springs to the vertices of the square lattice, but have deformed along the diagonals to form this  $c(4 \times 4)$  superlattice. The (nonprimitive) unit cell is indicated by the dashed lines.

$\bar{\phi}_{ij} = (\phi_{ij}^x, \phi_{ij}^y)$  and to reinstate the lattice constant  $\Delta$ . Then the Hamiltonian

$$\begin{aligned} \mathcal{H} = \sum_{i,j} [ & k\bar{\phi}_{ij}^2 - J\mu_{ij}(\mu_{i+1,j} + \mu_{i,j+1}) \\ & + J\alpha(\phi_{i+1,j}^x - \phi_{ij}^x - \Delta)\mu_{i+1,j}\mu_{ij} \\ & + J\alpha(\phi_{i,j+1}^y - \phi_{ij}^y - \Delta)\mu_{i,j+1}\mu_{ij} ] \end{aligned} \quad (2.5)$$

could lead to superlattices such as the one shown in Fig. 5. As with the one-dimensional models, we have required that the effective coupling constant increase in magnitude as the spins get closer, though we have not used the exact two-dimensional distance.<sup>32</sup> Similarly, a Hamiltonian with explicitly antiferromagnetic coupling ( $J < 0$ ) on a tri-

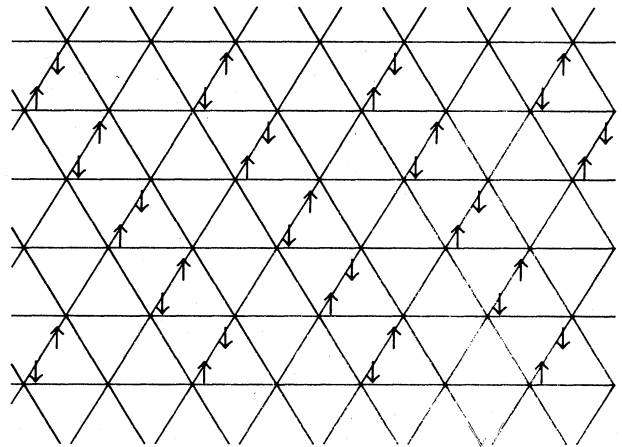


FIG. 6. A ground state of the deformable-triangular-lattice Ising antiferromagnet. The spins have deformed from the lattice sites (along the bonds) to eliminate frustration.

angular lattice could lead to the pattern displayed in Fig. 6. What is particularly noteworthy about this latter possibility is that the triangular-lattice antiferromagnet is the canonical example of a frustrated system.<sup>33</sup> Thus we see an example in which modulated order can arise out of a desire to *eliminate* frustration.

$$\mathcal{H} = \sum_{i,j,k} \{ k \phi_{ijk}^2 - J[(1-\alpha) - \alpha(\phi_{i,j,k+1} - \phi_{ijk})] \mu_{ijk} \mu_{i,j,k+1} - J_0(\mu_{ijk} \mu_{i+1,j,k} + \mu_{ijk} \mu_{i,j+1,k}) \}. \quad (2.6)$$

The deliberate choice of a uniaxial symmetry might, one would hope, make the Hamiltonian interesting in the context of graphite intercalation staging. However, it turns out to be sufficiently interesting in its own right that we will use it as a case study in extending our results to finite temperatures.

### III. SPIN-VARIABLE EQUIVALENT AND FINITE TEMPERATURE

An obvious approach to the statistical mechanics of any of the versions of the deformable-lattice model would be for us to integrate out the deformation coordinate, leaving an effective spin Hamiltonian. For the uniaxial example, Eq. (2.6), we can group the terms associated with each deformation,

$$\begin{aligned} \mathcal{H} = \sum_{i,j,k} [ & k \phi_{ijk}^2 - J \alpha \phi_{ijk} (\mu_{i,j,k+1} - \mu_{i,j,k-1}) \mu_{ijk} \\ & - J(1-\alpha) \mu_{ijk} \mu_{i,j,k+1} - J_0 \mu_{ijk} \mu_{i+1,j,k} \\ & - J_0 \mu_{ijk} \mu_{i,j+1,k} ], \end{aligned}$$

so that if we define a new deformation coordinate centered about an appropriate origin,

$$\xi_{ijk} = \phi_{ijk} - (J\alpha/2k)(\mu_{i,j,k+1} - \mu_{i,j,k-1}) \mu_{ijk}, \quad (3.1)$$

the Hamiltonian can be rewritten (to within an additive constant) as

$$\begin{aligned} \mathcal{H} = \sum_{i,j,k} ( & k \xi_{ijk}^2 - J_1 \mu_{ijk} \mu_{i,j,k+1} - J_2 \mu_{i,j,k-1} \mu_{i,j,k+1} \\ & - J_0 \mu_{ijk} \mu_{i+1,j,k} - J_0 \mu_{ijk} \mu_{i,j+1,k} ), \end{aligned} \quad (3.2a)$$

with the new coupling constants

$$J_1 \equiv J(1-\alpha), \quad (3.2b)$$

$$J_2 \equiv -(J\alpha)^2/(2k). \quad (3.2c)$$

Because the transformed deformations enter solely as a set of independent harmonic oscillators, they can now be integrated away, leaving us with an effective spin Hamiltonian

$$\begin{aligned} \mathcal{H} = - \sum_{i,j,k} ( & J_1 \mu_{ijk} \mu_{i,j,k+1} + J_2 \mu_{i,j,k-1} \mu_{i,j,k+1} \\ & + J_0 \mu_{ijk} \mu_{i+1,j,k} + J_0 \mu_{ijk} \mu_{i,j+1,k} ). \end{aligned} \quad (3.3)$$

An alternate approach to extending the deformable-lattice model to three dimensions would be to make it an *anisotropic* model. Suppose, in particular, we assume a simple-cubic lattice with deformations possible only along the  $z$  axis. If, otherwise, the model is simply an Ising model, then the Hamiltonian would be

However, Eq. (3.3) is nothing but the ANNNI model.<sup>1</sup> Along the  $z$  axis there are the ferromagnetic nearest-neighbor interactions ( $J_1 > 0$ ) and the antiferromagnetic next-nearest-neighbor interactions ( $J_2 < 0$ ) that are the signature of the standard formulation of the ANNNI Hamiltonian.

The implications of this equivalence are many. To begin with, the ground-state phase diagram (Fig. 3) can be (and actually was) calculated as that of the ANNNI model.<sup>34</sup> More to the point, the *finite-temperature* phase diagram, at least as far as the spin pattern is concerned, is also precisely that of the ANNNI model. Thus the phase diagrams already given in the previous paper<sup>1</sup> constitute predictions for modulated ordering in the deformable-lattice model (at two different levels of mean-field theory). Further, once we know the spin patterns, the corresponding deformations can be obtained (at any level of theory) by using the exact relation,

$$\langle \phi_i \rangle = (J\alpha/2k)(\langle \mu_{i-1} \mu_i \rangle - \langle \mu_i \mu_{i+1} \rangle), \quad (3.4)$$

which one can derive from the full partition function by inserting a generating field and taking the appropriate derivative. Equation (3.4) should, of course, be regarded as the finite-temperature generalization of Eq. (2.2), the equation for the ground-state deformations.

Even more important than these calculational considerations, however, is the new interpretation of the origin of modulated order afforded us by the equivalence of the ANNNI model and (one version of) the deformable-lattice model. Rather than attributing the modulation to competing forces,<sup>2</sup> we can regard the very same phases as resulting from a polarization effect. Interestingly, this reinterpretation means that spin Hamiltonians such as that of the ANNNI model may be thought of as *potentials of mean force*<sup>35</sup> instead of Hamiltonians and they therefore need not correspond to direct physical interactions. Note, for example, that the ANNNI model requires a next-nearest-neighbor term (which may or may not be appropriate to a given system) but the deformable lattice model has only nearest-neighbor interactions.

Because the deformable-lattice model can take on a variety of different forms, there are actually a number of different spin equivalents. One particularly intriguing case is the binary-variable ( $s=0,1$ ) generalization dealt with in Sec. II. The change from  $\mu$  ( $=\pm 1$ ) variables simply causes  $\mu$  to be replaced by  $s$  in Eq. (3.1), but when one completes the square in  $\phi$ , the resulting spin Hamiltonian

$$\mathcal{H} = - \sum_{i,j,k} [(J_1 - J_2) s_{ijk} s_{i,j,k+1} + J_2 s_{i,j,k-1} s_{ijk} s_{i,j,k+1} + J_0 s_{ijk} s_{i+1,j,k} + J_0 s_{ijk} s_{i,j+1,k} + H' s_{ijk}] \quad (3.5)$$

now involves a three-site interaction term. So, here again, we see that there may be difficult-to-understand spin-spin interactions which represent perfectly reasonable contributions to a microscopic Hamiltonian.

The mean-field theory of the binary model at the Bragg-Williams level<sup>36</sup> is defined by the free energy (aside from an additive constant)

$$-\beta F/N = N^{-1/3} \sum_k \left[ - \int_0^{2m_k-1} \tanh^{-1} x \, dx + \beta(J_1 - J_2) m_k m_{k+1} + \beta J_2 m_{k-1} m_k m_{k+1} + 2\beta J_0 m_k^2 + \beta H' m_k \right]$$

and the self-consistent equations for the magnetization

$$m_k \equiv \langle s_{ijk} \rangle = \frac{1}{2} + 2^{-1} \tanh\{(\beta/2)[(J_1 - J_2)(m_{k+1} + m_{k-1}) + J_2(m_{k+1} m_{k+2} + m_{k-1} m_{k+1} + m_{k-1} m_{k-2}) + 4J_0 m_k + H']\}.$$

However, we will not be discussing any of the numerical results from these equations, other than to mention that there are first- as well as second-order transitions present.<sup>37</sup> We, instead, want now to turn to a discussion of where we believe the whole class of models presented here fit in the broad context of studies of nontrivial ordering in solids.

#### IV. DISCUSSION

The distinguishing feature of the models presented in this paper is that they create modulated order through the interaction of two entirely different kinds of degrees of freedom. The pure spin models, such as the ANNNI model, end up creating patterns out of competing forces, whereas the purely elastic models, such as the Frenkel-Kontorova models, get patterns from competing periodicities.<sup>2</sup> Yet, in both cases, one is building in competing length scales at the start of the problem—in the ANNNI example by requiring forces of longer range than nearest neighbor.

The deformable-lattice models, on the other hand, produce a modulated structure from a polarization mechanism. A spin variable can polarize its environment via the deformations and the environment can feed back and stabilize the spins. There is therefore no need to build the different length scales into the Hamiltonian, and, consequently, one can limit the interactions to being nearest neighbor in character. In view of the existence of spin-variable equivalents to the deformable-lattice models which do not possess this desirable property, it may well be worthwhile to go back and reexamine some of the spin models in the literature to see whether they can indeed be reinterpreted as potentials of mean force for some shorter-ranged Hamiltonian. The Safran model for graphite intercalation staging<sup>7</sup> is an example which comes to mind.

In the same vein, it has been established that three-body forces are often needed in order to explain the structure of species chemisorbed on surfaces.<sup>38</sup> Some recent experimental cluster studies, in which pairs of adsorbed atoms repel but triplets attract,<sup>39</sup> seem to bear this idea out in a dramatic fashion. Yet, again, one wonders whether the forces between adatoms are mediated solely by a static surface or whether, instead, the surface deforms in

response to the adatoms, giving rise to an effective interaction. It is hard to avoid noticing that even the crude lattice-gas model discussed in this paper leads directly to three-body forces, Eq. (3.5). Intriguingly, these three-body forces are explicitly repulsive, since  $J_2 < 0$ , but the net energy of a cluster of three collinear atoms (1,2,3) in this model,

$$\epsilon_{123} = -2(J_1 - J_2) - J_2 = -2J_1 + J_2,$$

is still lower than that predicted by adding the two unperturbed pair interactions (without deformations),

$$\epsilon_{12} + \epsilon_{23} = -J_1 - J_1 = -2J_1.$$

In fact, if the deformation is large enough,  $\epsilon_{123}$  itself is always negative, so this very model would predict that a triplet of adatoms could be stable even if individual pairs of atoms repelled ( $J_1 < 0$ ).

Of course, one should not make too much of the specific details of the models proposed in this paper. It may be worth pointing out that the particular Hamiltonian we chose to study here, Eq. (2.1), differs mathematically from the Baker-Essam<sup>21</sup> and Chen-Kardar<sup>25</sup> Hamiltonians only by the apparently trivial replacement discussed in Sec. II. Of course, this distinction did turn out to be enough to make these latter models irrelevant to modulated-order problems (though they were very important in thinking about the Fisher renormalization of critical exponents<sup>40</sup>). The mathematical straightforwardness of our model is also revealed by the observation that in going from an Ising model with a fluctuating coupling constant, Eq. (2.6), to the ANNNI model, Eq. (3.3), we are simply generalizing the time-honored Hubbard-Stratonovich transformation,<sup>41</sup> which converts a paramagnet in a fluctuating field into a standard Ising model.<sup>42</sup>

Briefly, the partition function of any system of noninteracting Ising spins,  $\mu = \{\mu_1, \dots, \mu_N\}$ ,

$$Z(\mathbf{h}) = \sum_{\mu} \exp \left[ \beta \sum_j h_j \mu_j \right] \equiv \sum_{\mu} e^{\beta \mathbf{h} \cdot \mu},$$

can be turned into the partition function for a fully interacting Ising model if the magnetic fields at each site,  $\mathbf{h} = \{h_1, \dots, h_N\}$ , are considered to be proportional to some set of harmonically fluctuating variables,  $\mathbf{x}$ . In particular, if we define

$$\mathbf{h} = (4\pi/\beta)^{1/2} \mathbf{J}^{1/2} \cdot \mathbf{x},$$

then completing the square reveals that

$$Q = \int d\mathbf{x} e^{-\pi\mathbf{x}^2} Z(\mathbf{h}) = \sum_{\mu} e^{\beta\mu \cdot \mathbf{J} \cdot \mu} \\ = \sum_{\mu} \exp \left[ \beta \sum_{j,k} \mu_j J(j,k) \mu_k \right]$$

for any spin-spin interaction,  $J(j,k)$ . All we have done in this paper is to repeat this process, but with the *interactions* now allowed to fluctuate in a suitably chosen fashion.

Nevertheless, the physics revealed by these elementary transformations is still of some consequence. In particular, the interpretation of our Hamiltonian as that of an Ising model with a distribution of interaction strengths means that we can rigorously think of the ANNNI model as an *annealed random magnet*.<sup>43,44</sup> The coupling-constant distribution is certainly a highly correlated one,<sup>45</sup> but it is just this correlation which makes inappropriate the common attitude that annealed random magnets are uninteresting. Indeed, it is the correlations between effective coupling constants implicit in the distribution which leads to the modulation.

While this aspect does complicate the analogy somewhat, it is still tempting to ask what similarities there might be between the ANNNI model (in its annealed random magnet guise) and a quenched random magnet, such as a spin glass.<sup>27</sup> Without belaboring it too much, we note that the width of the coupling-constant distribution in the ANNNI model will be proportional to  $k^{-1}$ , which, from Eqs. (3.2b) and (3.2c), means that it is proportional to  $\kappa$  ( $= -J_2/J_1$ ). Thus, one might expect that a phase diagram for the ANNNI model plotted as  $T$  versus  $\kappa^{-1}$  might look similar to a spin-glass phase diagram plotted as  $T$  versus reciprocal coupling-constant distribution width. The results, shown in Fig. 7, are indeed roughly

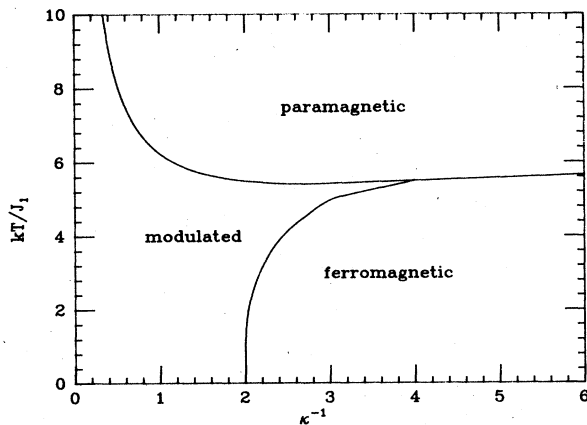


FIG. 7. Finite-temperature ANNNI phase diagram, in Bragg-Williams mean-field theory (Ref. 1), plotted vs  $\kappa^{-1}$ . By the words "paramagnetic," "ferromagnetic," and "modulated," we are referring to the disordered, uniformly ordered, and nonuniformly ordered phases, respectively. In our interpretation of the ANNNI model as a random magnet, this figure is analogous to the spin-glass phase diagram (Fig. 1) of Ref. 46.

analogous: the paramagnetic, ferromagnetic, and modulated phases of the ANNNI model appear in the same locations as the paramagnetic, ferromagnetic, and spin-glass phases of the Sherrington-Kirkpatrick model.<sup>46</sup>

We should emphasize that this analogy is certainly *not* meant to be a literal one. It does suggest, however, that annealed random magnets are not as bereft of interest as is often supposed. Because they are relatively easy to work with and interpret, they may even be a reasonable place to try to study the physics of quenched amorphous materials.<sup>47</sup>

#### ACKNOWLEDGMENTS

We would like to thank Steven G. Desjardins for discussions leading to this line of investigation and Peder Estrup for valuable comments on possible applications to surface physics. This work was supported by NSF Grant No. CHE-81-21474.

#### APPENDIX: DETERMINATION OF A GROUND-STATE PHASE DIAGRAM

As discussed in Sec. III, the easiest way to find the ground states of the lattice-gas version of the deformable-lattice model, Eq. (2.4), is to work with the equivalent spin Hamiltonian, Eq. (3.5). Since the in-plane interactions are exclusively ferromagnetic, in the ground state all in-plane spins will be aligned. The ground states can therefore be found from the one-dimensional Hamiltonian,

$$\mathcal{H} = - \sum_j [(J_1 - J_2)s_j s_{j+1} + J_2 s_{j-1} s_j s_{j+1} + H s_j], \quad (\text{A1})$$

where  $s_j = 0$  or 1, and the couplings  $J_1$  and  $J_2$  are given in terms of the deformable-lattice-model parameters by Eq. (3.2).

We will find the ground states by an enumeration approach similar to that of Morita and Horiguchi,<sup>34</sup> who investigated the ground states of the ANNNI model. The energy of an arbitrary pattern will be written in terms of a set of structural variables, and the ground state will be determined by minimizing the energy with respect to these variables.

Consider an arbitrary pattern,  $P$ , of occupied (+) and unoccupied (0) sites. Our first two structural variables are  $n_+$  defined as the number of + sites with two + neighbors, and  $n_0$  the number of 0 sites with two 0 neighbors. The energy of  $P$  can be written as

$$E = E' + n_+ \epsilon_+, \quad (\text{A2})$$

where  $E'$  is the energy of a pattern  $P'$ , formed from  $P$  by removing the  $n_+$  occupied sites and  $n_0$  unoccupied sites described above. The contribution, per site, of the sites removed is

$$\epsilon_0 \equiv 0,$$

$$\epsilon_+ \equiv -J_2 - (J_1 - J_2) - H = -J_1 - H.$$

By design,  $P'$  can always be constructed from the groups

+0, +00, ++0, ++00 .

The contribution of each group to  $E'$ , per site, is

$$\epsilon_{+0} = -H/2 ,$$

$$\epsilon_{+00} = -H/3 ,$$

$$\epsilon_{++0} = [-(J_1 - J_2) - 2H]/3 ,$$

$$\epsilon_{++00} = [-(J_1 - J_2) - 2H]/4 .$$

Define the structural variables,  $n_{+0}$ ,  $n_{+00}$ ,  $n_{++0}$ , and  $n_{++00}$ , as the number of times each group appears in  $P'$ . Then, from Eq. (A2), the energy of the original pattern  $P$  is

$$E = n_+ \epsilon_+ + 2n_{+0} \epsilon_{+0} + 3n_{+00} \epsilon_{+00} + 3n_{++0} \epsilon_{++0} + 4n_{++00} \epsilon_{++00} . \quad (\text{A3})$$

This energy must now be minimized with respect to the structural variables, with the proviso that these variables be consistent with a fixed number of sites  $N$ :

$$N = n_0 + n_+ + 2n_{+0} + 3n_{+00} + 3n_{++0} + 4n_{++00} . \quad (\text{A4})$$

Equations (A3) and (A4) represent a trivial linear programming problem. Since all the terms in Eq. (A4) are

positive,  $E$  is bounded from below by  $N\epsilon_{\min}$ , where  $\epsilon_{\min}$  is the smallest of the energies per site appearing in Eq. (A3). Therefore, when the smallest energy per site is unique, the ground state is nondegenerate and requires

$$E = N\epsilon_{\min} .$$

The only possible nondegenerate ground states are

$$\cdots + + + + \cdots \quad \text{for } \epsilon_{\min} = \epsilon_+ ,$$

$$\cdots + 0 + 0 + 0 \cdots \quad \text{for } \epsilon_{\min} = \epsilon_{+0} ,$$

$$\cdots + + 0 + + 0 \cdots \quad \text{for } \epsilon_{\min} = \epsilon_{++0} ,$$

$$\cdots 000000 \cdots \quad \text{for } \epsilon_{\min} = \epsilon_0 .$$

Figure 4 shows the regions in the  $\kappa, H$  plane in which each phase is a ground state.

In the event that two or more  $\epsilon$ 's are equal, the ground state is degenerate. On the  $\epsilon_+ = \epsilon_0$  line, there are exactly two ground states. Any other phase boundary corresponds to an *infinite* degeneracy, because arbitrarily long domains of the two (or more) degenerate patterns can be alternated without changing the energy. Equivalently, one could say that domain walls now have no self-energy.

\*Present address: Department of Physics, Brown University, Providence, RI 02912.

<sup>1</sup>T. DeSimone and R. M. Stratt, preceding paper, Phys. Rev. B **32**, 1537 (1985).

<sup>2</sup>P. Bak, Rep. Prog. Phys. **45**, 587 (1982).

<sup>3</sup>M.E. Fisher and D. A. Huse, in *Melting, Localization and Chaos*, edited by R. K. Kalia and P. Vashishta (Elsevier, New York, 1982), p. 259.

<sup>4</sup>R. J. Elliott, Phys. Rev. **124**, 346 (1961); also see Ref. 1 and the references therein.

<sup>5</sup>M. S. Dresselhaus and G. Dresselhaus, Adv. Phys. **30**, 139 (1981); S. A. Solin, Adv. Chem. Phys. **49**, 455 (1982).

<sup>6</sup>R. Nishitani, Y. Uno, and H. Suematsu, Phys. Rev. B **27**, 6572 (1983).

<sup>7</sup>S. A. Safran, Phys. Rev. Lett. **44**, 937 (1980); S. A. Safran, Synth. Met. **2**, 1 (1980); P. Hawrylak and K. R. Subbaswamy, Phys. Rev. B **28**, 4851 (1983).

<sup>8</sup>S. E. Millman and G. Kirzenow, Phys. Rev. B **28**, 3482 (1983); W. R. McKinnon and R. R. Haering, Solid State Ionics **1**, 111 (1980); S. A. Safran and D. R. Hamman, Phys. Rev. Lett. **42**, 1410 (1979).

<sup>9</sup>P. Bak and J. von Boehm, Phys. Rev. B **21**, 5297 (1980).

<sup>10</sup>D. Huse, Phys. Rev. B **24**, 5180 (1981); S. Ostlund, *ibid.* **24**, 398 (1981). Another exception is discussed by E. Domany and B. Schaub [Phys. Rev. B **29**, 4095 (1984)].

<sup>11</sup>E. Matsushita, K. Yoshimitsu, and T. Matsubara, Prog. Theor. Phys. **64**, 1176 (1980).

<sup>12</sup>J. Frenkel and T. Kontorova, J. Phys. (Moscow) **1**, 137 (1939).

<sup>13</sup>F. C. Frank and J. H. van der Merwe, Proc. R. Soc. London **198**, 205 (1949).

<sup>14</sup>S. Aubry, J. Phys. (Paris) **44**, 147 (1983).

<sup>15</sup>Other studies of the Frenkel-Kontorova model include S. N. Coppersmith and D. S. Fisher, Phys. Rev. B **28**, 2566 (1983);

H. U. Beyeler, L. Pietronero, and S. Strässler, *ibid.* **22**, 2988 (1980); L. Pietronero, W. R. Schneider, and S. Strässler, *ibid.* **24**, 2187 (1981). The latter two are interesting in our context because they construct a spin Hamiltonian approximately equivalent to the Frenkel-Kontorova model.

<sup>16</sup>R. E. Peierls, *Quantum Theory of Solids* (Clarendon, Oxford, 1955), p. 108.

<sup>17</sup>W. P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. Lett. **42**, 1698 (1979); Phys. Rev. B **22**, 2099 (1980).

<sup>18</sup>S. N. Dixit and S. Mazumdar, Phys. Rev. B **29**, 1824 (1984).

<sup>19</sup>D. C. Mattis and T. D. Schultz, Phys. Rev. **129**, 175 (1963).

<sup>20</sup>H. Wagner, in *Hydrogen in Metals I*, edited by G. Alefeld and J. Völkl (Springer, Berlin, 1978), p. 5.

<sup>21</sup>G. A. Baker, Jr. and J. W. Essam, Phys. Rev. Lett. **24**, 447 (1970); J. Chem. Phys. **55**, 861 (1971).

<sup>22</sup>V. G. Vaks and A. I. Larkin, Zh. Eksp. Teor. Fiz. **49**, 975 (1965) [Sov. Phys.—JETP **22**, 678 (1966)]; A. I. Larkin and S. A. Pikin, *ibid.* **56**, 1664 (1969) [29, 891 (1969)].

<sup>23</sup>L. Gunther, D. J. Bergman, and Y. Imry, Phys. Rev. Lett. **27**, 558 (1971).

<sup>24</sup>D. J. Bergman and B. I. Halperin, Phys. Rev. B **13**, 2145 (1976).

<sup>25</sup>Z. Y. Chen and M. Kardar, Phys. Rev. B **30**, 4113 (1984). These authors find both isotropic and anisotropic antiferromagnetism.

<sup>26</sup>S. K. Sinha, *Ordering in Two Dimensions* (North-Holland, New York, 1980).

<sup>27</sup>*Ill-Condensed Matter*, edited by R. Balian, R. Maynard, and G. Toulouse (North-Holland, Amsterdam, 1977).

<sup>28</sup>N. Caswell, S. A. Solin, T. M. Hayes, and S. J. Hunter, Physica **99B**, 463 (1980). These authors observe puckering of the graphitic layers near the intercalate atoms. This type of local distortion should be distinguished from the long-range elastic



- distortion considered in Ref. 8.
- <sup>29</sup>Among the examples in which the sign of the interaction varies with distance are Ruderman-Kittel-Kasuya-Yoshida-type interactions. See, for example, T. L. Einstein and J. R. Schrieffer, *Phys. Rev. B* **7**, 3629 (1973).
- <sup>30</sup>A good example of polarization phenomena is described in R. P. Feynman, *Statistical Mechanics* (Benjamin, Reading, 1972), Chap. 8.
- <sup>31</sup>Note that changing to lattice-gas variables does *not* correspond simply to a shift in the field. (See Fig. 4 and the discussion in Sec. III.)
- <sup>32</sup>A more literal translation of the one-dimensional linear dependence on distance,  $|\bar{\phi}_{jk} - \bar{\phi}_{lm}|$ , would, in fact, be nonlinear in the components  $\phi_x$  and  $\phi_y$ .
- <sup>33</sup>G. Toulouse and J. Vannimenus, *Recherche* **8**, 980 (1977).
- <sup>34</sup>T. Morita and T. Horiguchi, *Phys. Lett.* **38A**, 223 (1972).
- <sup>35</sup>We are using the phrase "potential of mean force" as is commonly done in the chemical literature: the argument of the Boltzmann factor remaining after *rigorously* integrating out selected degrees of freedom. See, for example, D. L. Goodstein [*States of Matter* (Prentice-Hall, Englewood Cliffs, NJ, 1975), p. 249] and D. A. McQuarrie [*Statistical Mechanics* (Harper and Row, New York, 1976), p. 266]. The Boltzmann factor of the potential of mean force is similar in concept to that of an influence functional, as used in R. P. Feynman and A. R. Hibbs [*Quantum Mechanics and Path Integrals* (McGraw-Hill, New York, 1965), p. 343], but should be clearly distinguished from the spin Hamiltonians of Ref. 15 in which elastic degrees of freedom were approximately turned into spin degrees of freedom.
- <sup>36</sup>The defining equations for the standard, or Bragg-Williams level, mean-field theory for systems with modulated order are given by Eqs. (2.33) and (2.34) of Ref. 1.
- <sup>37</sup>L. D. Landau and E. M. Lifshitz, *Statistical Physics, Part 1* (Pergamon, Oxford, 1980), p. 459.
- <sup>38</sup>L. D. Roelofs and P. J. Estrup, *Surf. Sci.* **125**, 51 (1983).
- <sup>39</sup>H.-W. Fink and G. Erlich, *J. Chem. Phys.* **81**, 4657 (1984).
- <sup>40</sup>M. E. Fisher, *Phys. Rev.* **176**, 257 (1968).
- <sup>41</sup>J. Hubbard, *Phys. Rev. Lett.* **3**, 77 (1959).
- <sup>42</sup>B. Mühlischlegel, in *Path Integrals*, edited by G. J. Papadopoulos (Plenum, New York, 1978), p. 383.
- <sup>43</sup>M. F. Thorpe and D. Beeman, *Phys. Rev. B* **14**, 188 (1976).
- <sup>44</sup>R. B. Stinchcombe, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, London, 1983), Vol. 7, p. 151.
- <sup>45</sup>The word "correlated" is used here in the sense of Ref. 44: the *a priori* distribution of coupling constants does not factor into independent contributions for each spin-spin interaction.
- <sup>46</sup>D. Sherrington and S. Kirkpatrick, *Phys. Rev. Lett.* **35**, 1792 (1975).
- <sup>47</sup>G. Toulouse, *Phys. Rep.* **67**, 47 (1980).