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Soluble Model of Interacting Classical Quadrupoles in One Dimension*

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We solve exactly for the thermodynamic properties of a linear chain of classical spins with near-neighbor bilinear and biquadratic isotropic exchange interactions. At zero temperature the system can be either ordered or disordered, depending on the relative magnitudes and signs of the bilinear and biquadratic exchange. In addition, it is found that at finite temperatures "disorder points" occur, at which the correlation functions change in character from monotonic decreasing functions of distance to oscillatory functions. The disorder points found here are of interest because they occur even though the interactions are restricted to nearest neighbors.

I. INTRODUCTION

We study the statistical mechanics of a linear chain of classical spins interacting with the Hamiltonian

$$\mathcal{H} = J_1 \sum_i \vec{S}_i \cdot \vec{S}_{i+1} + J_2 \sum_i (\vec{S}_i \cdot \vec{S}_{i+1})^2 . \tag{1}$$

Here $\vec{S}_i$ is a unit vector at the ith site in the chain with components S_i^x, S_i^y, S_i^z. It is well known that such one-dimensional nearest-neighbor systems cannot exhibit long-range order at nonzero temperatures and as such they are of limited interest. Long-range order may appear at $T=0$, however, and in some sense a phase transition may be said to occur there. The Hamiltonian (1) is of interest in this case because for a range of positive values of J_2 the system does not order even at $T=0$, and a study of this regime illustrates the mathematical mechanism of the phase transition. The statistical-mechanical properties of (1) with $J_2 = 0$ were first studied by Fisher.[1] Later, Joyce[2] derived these properties by using the transfer-matrix method. A straightforward application of this method enables us to solve for the properties of (1), and this is done in the following sections.

Hamiltonians of the form of (1) arise in magnetism. The biquadratic term J_2 is ordinarily small in systems where the orbital motion is quenched, but can be large in systems where the orbital motion is important and where a pseudospin formalism is used to describe the energy levels.[3] Also, a treatment of orientational transitions in molecular crystals[4] has been based on a three-dimensional form of Eq. (1), and, with $J_1 = 0$, Eq. (1) may be used to describe the interaction between atoms in liquid crystals. In studying (1) it is necessary to consider, besides the usual "magnetic" order parameter $M = \langle S_i^z \rangle$, the "quadrupolar" order parameter $Q = \frac{1}{2}\langle 3(S_i^z)^2 - 1 \rangle$, since the biquadratic term can cause order of this type while it does not directly produce magnetic order.[5] The interplay of these two order parameters can be seen even in the simple one-dimensional model treated here.

Another point of interest of this model is that it exhibits a disorder point of the second kind, as defined (following Widom and Fisher) by Stephenson,[6] for a range of positive values of J_2 [when the two terms in (1) "compete"]. The disorder point is, in this case, a temperature T_Δ at which the quadrupole-quadrupole near-neighbor correlation function changes sign. Below T_Δ, the correlations decrease monotonically with distance, while above this temperature they have an oscillatory behavior with a temperature-independent wavelength equal to twice the nearest-neighbor separation. The disorder points occur whether or not the system orders at $T=0$, and, for a small range of parameters J_1 and J_2, two disorder points are found.

Stephenson[6] has given several examples of disorder points in Ising models with competing nearest-neighbor and next-nearest-neighbor interactions. The system considered here differs from those discussed by Stephenson in that the interactions here are between nearest neighbors only and the spins have a continuous range of variation. We conclude, however, that the presence of the disorder points is, in all cases, a consequence of competition between two "kinematically coupled" order parameters, i.e., two order parameters one of which cannot be varied arbitrarily without affecting the other. The cases considered by Stephenson are the magnetization and the sublattice magnetization, while in our model the order parameters are those mentioned above, i.e., the magnetization (dipolar order) and the quadrupolar order.

In the following sections we calculate the free-energy and the correlation functions. We then discuss the ground-state properties and, finally, the thermal properties and disorder points.

II. FREE-ENERGY AND CORRELATION FUNCTIONS

A. Partition Function

All thermodynamic quantities can be obtained from the partition function, which is most directly evaluated in terms of the eigenvalues of the transfer kernel. As shown by Domb,[7] the partition function for a chain of N spins is given by

$$Z=\sum_{n=0}^{\infty}\lambda_n^N\,, \tag{2}$$

where the quantity λ_n is the nth eigenvalue of the integral equation

$$\lambda_n\psi_n(\vec{S}_2)=\int\frac{d\vec{S}_1}{4\pi}\,e^{-\beta H_{12}}\,\psi_n(\vec{S}_1)\,, \tag{3}$$

with, in our case, $H_{12}=J_1\vec{S}_1\cdot\vec{S}_2+J_2(\vec{S}_1\cdot\vec{S}_2)^2$. In the thermodynamic limit $N\rightarrow\infty$, we need only the largest eigenvalue λ_0, and $Z\sim\lambda_0^N$.

It is easily seen that the eigenfunctions of (3) are the spherical harmonics[8] as long as H_{12} is a function only of the scalar product $\vec{S}_1\cdot\vec{S}_2$. This is, of course, the case for the Hamiltonian (1). Setting $\vec{S}_1\cdot\vec{S}_2=\cos\theta_{12}$ we have

$$\exp(-\beta J_1\cos\theta_{12}-\beta J_2\cos^2\theta_{12})=\sum_{l=0}^{\infty}(2l+1)\,\lambda_l P_l(\cos\theta_{12})\,, \tag{4}$$

where λ_l are the coefficients obtained by expanding in terms of Legendre polynomials. They are given by

$$\lambda_l=\tfrac{1}{2}\int_{-1}^{+1}e^{-\beta J_1x-\beta J_2x^2}\,P_l(x)\,dx\,. \tag{5}$$

Using the addition theorem we have

$$P_l(\cos\theta_{12})=\frac{4\pi}{2l+1}\sum_m Y_{lm}(\vec{S}_1)\,Y_{lm}^*(\vec{S}_2)\,, \tag{6}$$

where $\vec{S}_1$ and $\vec{S}_2$ are referred to arbitrary axes, we see that

$$e^{-\beta H_{12}}=4\pi\sum_{lm}\lambda_l Y_{lm}(\vec{S}_1)\,Y_{lm}^*(\vec{S}_2)\,. \tag{7}$$

Inserting (7) into the eigenvalue equation (3) and using the orthonormality properties of the spherical harmonics we verify that the λ_l of Eq. (5) are also the eigenvalues of (3), and the eigenfunctions are the spherical harmonics $Y_{lm}(\vec{S}_i)$. The largest eigenvalue clearly occurs for $l=0$, and can be expressed in terms of the error function[9]:

$$\lambda_0=\tfrac{1}{4}\left(\frac{\pi}{\beta J_2}\right)^{1/2}e^{\beta J_1^2/4J_2}\left\{\operatorname{erf}\left[(\beta J_2)^{1/2}\left(1+\frac{J_1}{2J_2}\right)\right]+\operatorname{erf}\left[(\beta J_2)^{1/2}\left(1-\frac{J_1}{2J_2}\right)\right]\right\}\,. \tag{8}$$

Note that the partition function and hence the free energy is a function of J_1^2. The operation $J_1\rightarrow -J_1$ is equivalent to letting $\vec{S}_i\rightarrow-\vec{S}_i$ at every other site along the chain. It is a unitary operation in the classical-spin case and therefore allowable; this is not true for quantum spins, of course.

It is worth observing that a more general isotropic Hamiltonian like (1), but containing additional terms $\sum_i(\vec{S}_i\cdot\vec{S}_{i+1})^n$, would also have eigenfunctions $Y_{lm}(\vec{S}_i)$ but different eigenvalues λ_l.

B. Correlation Functions

The thermal average of two quantities α_i and α'_{i+r}, which are functions of the spin vectors at i and $i+r$, can also be expressed in terms of the eigenvalues λ_l of the transfer matrix. We have

$$\langle\alpha_i\alpha'_{i+r}\rangle=\frac{1}{Z}\int\cdots\int\frac{d\vec{S}_i\cdots d\vec{S}_N}{(4\pi)^N}\times e^{-\beta H_{12}}\cdots e^{-\beta H_{i-1,i}}\,\alpha_i\cdots\alpha'_{i+r}\cdots e^{-\beta H_{N1}}\,. \tag{9}$$

Using the expansions (4) and (5) and the orthogonality of the spherical harmonics we have in the limit $N\rightarrow\infty$

$$\langle\alpha_i\alpha'_{i+r}\rangle=\sum_{lm}\left(\frac{\lambda_l}{\lambda_0}\right)^r\left(\int d\vec{S}_i\,Y_{00}^*(\vec{S}_i)\,\alpha_iY_{lm}(\vec{S}_i)\right)\times\left(\int d\vec{S}_{i+r}\,Y_{lm}^*(\vec{S}_{i+r})\alpha'_{i+r}\,Y_{00}(\vec{S}_{i+r})\right). \tag{10}$$

Of particular interest in the present case are

$$\langle\vec{S}_i\cdot\vec{S}_{i+r}\rangle=(\lambda_1/\lambda_0)^r\,, \tag{11}$$

$$\langle\tfrac{3}{2}(\vec{S}_i\cdot\vec{S}_{i+r})^2-\tfrac{1}{2}\rangle=(\lambda_2/\lambda_0)^r\,. \tag{12}$$

Both the correlation functions (11) and (12) have the property that they vanish at infinite temperature and become equal to ±1 if the ground state is ordered. It is easy to see from (5) and (11) that the nearest-neighbor dipolar correlation function $\langle\vec{S}_i\cdot\vec{S}_{i+1}\rangle$ always has the sign of $-J_1$, i.e., $J_1\langle\vec{S}_i\cdot\vec{S}_{i+1}\rangle\leq0$ and so there can be no dipolar disorder point. This is not the case for the quadrupolar correlation function (12) since (λ_2/λ_0) may change sign as a function of temperature and quad-

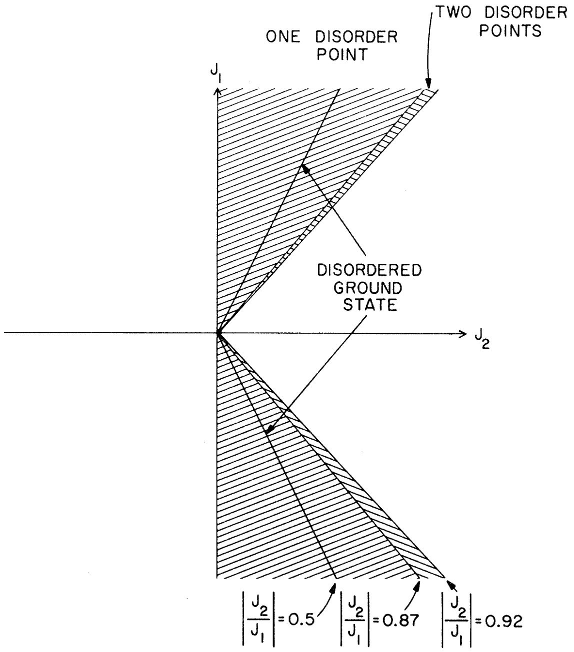

FIG. 1. Solid lines $|J_2/J_1| = 0.5$ for positive J_2 divide the ordered and disordered regimes at $T = 0$, which lie on the left- and right-hand sides of the diagram, respectively. The lightly shaded region, which covers both kinds of $T = 0$ regimes, has ond disorder point in the quadrupolar correlation function. The heavily shaded region, which lies entirely in the disordered $T = 0$ regime, has two disorder points in the quadrupolar correlation function and lies in the wedges defined by $0.87 < |J_2/J_1| < 0.92$ for positive J_2.

rupolar disorder points do exist. It is useful to define a dipolar correlation length R_D and a quadrupolar correlation length R_Q by

$$1/R_D = -\ln|\lambda_1/\lambda_0| \tag{13}$$

and

$$1/R_Q = -\ln|\lambda_2/\lambda_0| \, , \tag{14}$$

so that (11) and (12) may be written

$$|\langle \vec{S}_i \cdot \vec{S}_{i+r} \rangle| = e^{-r/R_D}, \tag{15}$$

$$|\langle \tfrac{3}{2}(\vec{S}_i \cdot \vec{S}_{i+r})^2 - \tfrac{1}{2} \rangle| = e^{-r/R_Q}. \tag{16}$$

These definitions of the correlation lengths R_D and R_Q allow both for the case when the correlations decrease monotonically with distance and the case when they decay in an oscillatory manner. We note also that the more general interactions mentioned at the end of Sec. II A could produce dipolar disorder points as well.

III. GROUND-STATE PROPERTIES

The ground state is obtained by putting $\vec{S}_i \cdot \vec{S}_{i+1} = \cos\theta$ in the Hamiltonian (1) and minimizing the energy with respect to θ. The result is shown in Fig. 1. From $J_2/J_1 = 0.5$ moving in a counterclockwise direction to $J_2/J_1 = 0.5$, the ground state is ordered with all the even eigenvalues λ_0, λ_2, λ_4, etc., being 1 and all the odd eigenvalues λ_1, λ_3, λ_5, etc., being -1 if J_1 is positive, 0 if J_1 is zero, and 1 if J_1 is negative. In this region the spins align either parallel or antiparallel and long-range order exists.

The rest of the area in the J_1, J_2 plane in Fig. 1 represents a disordered ground state in which $\cos\theta = -J_1/2J_2$ and there is no long-range order.

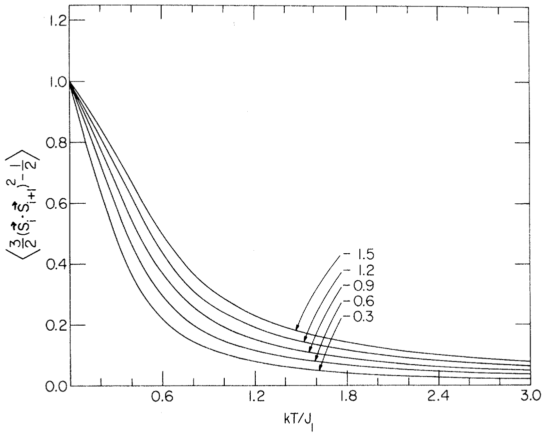

FIG. 2. Nearest-neighbor quadrupolar correlation function $\langle \frac{3}{2}(\vec{S}_i \cdot \vec{S}_{i+1})^2 - \frac{1}{2} \rangle$ plotted as a function of temperature $1/\beta J_1 = kT/J_1$ for negative J_2 and $J_2/J_1 = -0.3$, -0.6, -0.9, -1.2, -1.5.

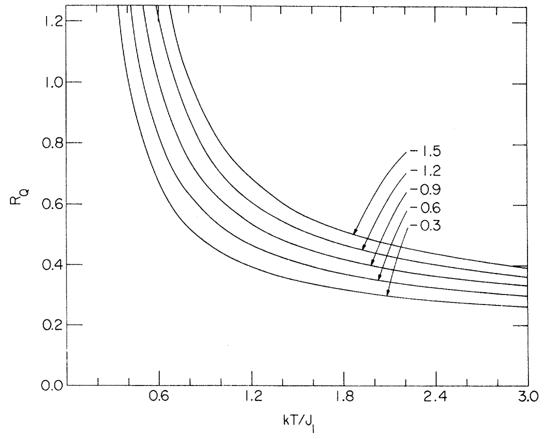

FIG. 3. Quadrupolar correlation length R_Q plotted against temperature $1/\beta J_1$ for negative J_2 and $J_2/J_1 = -0.3$, -0.6, -0.9, -1.2, -1.5. R_Q goes to ∞ at zero temperature, corresponding to an ordered ground state.

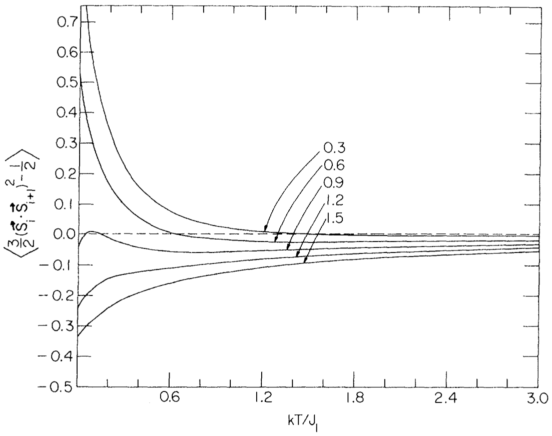

FIG. 4. Nearest-neighbor quadrupolar correlation function $\langle \frac{3}{2}(\vec{S}_i \cdot \vec{S}_{i+1})^2 - \frac{1}{2} \rangle$ plotted as a function of temperature $1/\beta J_1$ for positive J_2 and $J_2/J_1 = 0.3$, 0.6, 0.9, 1.2, 1.5. The curves cross the x axis at the disorder points, either 0, 1, 2 times for $J_2/J_1 = 1.5$, 1.2, 0.9, 0.6, 0.3, respectively.

The reason no long-range order can exist is well illustrated by the case $J_1 = 0$ where $\theta = \frac{1}{2}\pi$ or 3π. Clearly, there are many ways of arranging a linear chain of spins so that the angle between neighbors is $\frac{1}{2}\pi$ or $\frac{3}{2}\pi$ and spins far apart will only be weakly correlated. This "packing problem" is similar to that which occurs in the two-dimensional triangular-net Ising model[10] which orders when the interactions are ferromagnetic but has a finite entropy at $T = 0$ when the interactions are antiferromagnetic. In this region, the other eigenvalues are given by $\lambda_l = P_l(-J_1/2J_2)$ and $|\lambda_l \lambda_0| < 1$, so that there is no eigenvalue degeneracy in the disordered region.

IV. THERMAL PROPERTIES

As was stated in Sec. III, the dipolar correlation function $\langle \vec{S}_i \cdot \vec{S}_{i+1} \rangle$ does not change sign as a function of temperature. It goes from its zero-temperature value to zero to high temperatures. The dipolar correlation length R_D has a finite value at $T = 0$ in the disordered region and is infinite at $T = 0$ in the ordered region: In both cases it goes to zero as the temperature goes to infinity. The behavior associated with the dipolar correlation function is therefore rather uninteresting and we shall not pursue it further.

On the other hand, the quadrupolar correlation function $\langle \frac{3}{2}(\vec{S}_i \cdot \vec{S}_{i+1})^2 - \frac{1}{2} \rangle$ can go through zero at finite temperatures. As $\langle \frac{3}{2}(\vec{S}_i \cdot \vec{S}_{i+1})^2 - \frac{1}{2} \rangle$ is a function of J_1^2 we only consider positive J_1. In Fig. 2 we show the quadrupolar correlation function for nearest neighbors plotted against temperature for negative J_2 and various values of J_2/J_1. The correlation function goes to 1 at zero temperature, showing from (12) that $\lambda_2 = \lambda_0$, and we have an ordered ground state. As the temperature is increased the correlations go smoothly to 0. In Fig. 3, we show the quadrupolar correlation length R_Q as a function of temperature, calculated from (14). At low temperature R_Q goes to infinity and as the temperature is increased it goes smoothly to 0. We see, therefore, that there are no disorder points when J_2 is negative. This is because the quadrupolar term in (1) wants to align the spins parallel or antiparallel and the dipolar term determines which configuration is stable. There is therefore no competition between the two terms. This is not the case when J_2 is positive since then the quadrupolar term wants to put the spins at right angles, whereas the dipolar term wants to have them either parallel or antiparallel. This competition can favor one term in one temperature regime and the other in another temperature regime, thus leading to a disorder point.

In Fig. 4, we plot the quadrupolar correlation function against temperature for positive J_2 and various values of J_2/J_1. We see that the correlation function can indeed go through zero, once for $J_2/J_1 = 0.3$, 0.6; twice for $J_2/J_1 = 0.9$; there is no disorder point for $J_2/J_1 = 1.2$, 1.5. Figure 5 shows the correlation length R_Q as a function of temperature and it can be clearly seen where the correlation length goes to 0 giving a cusplike appearance. This is very similar to the behavior found by Stephenson[6] for a one-dimensional Ising model with competing nearest- and next-nearest-neighbor interactions. When $\langle \frac{3}{2}(\vec{S}_i \cdot \vec{S}_{i+1})^2 - \frac{1}{2} \rangle = (\lambda_2/\lambda_0)$ is negative, the quadrupolar correlations (12) decay in an oscillatory way with distance, changing sign at each site. This corresponds to a wavelength of twice the nearest-neighbor separation. This de-

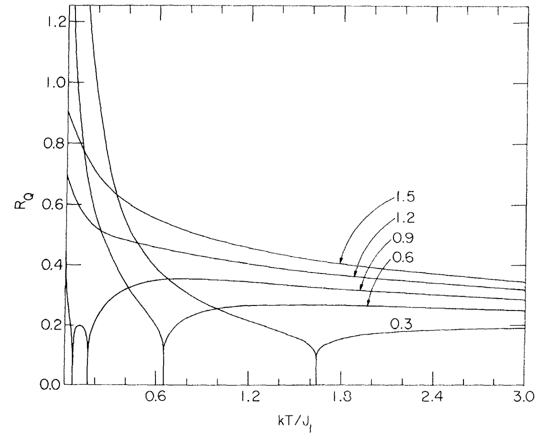

FIG. 5. Quadrupolar correlation length R_Q plotted against temperature $1/\beta J_1$ for $J_2/J_1 = 0.3$, 0.6, 0.9, 1.2, 1.5. R_Q goes to zero at the disorder points and goes to ∞ if the ground state is ordered and a finite value if it is disordered.

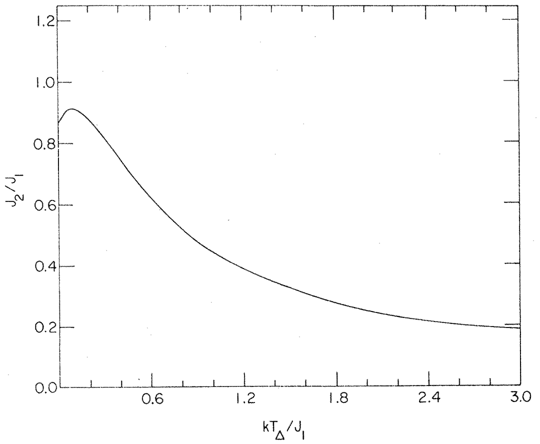

FIG. 6. Plot of the disorder temperature kT_D/J_1 against J_2/J_1 for J_2 positive. T_Δ is defined as the temperature at which $R_Q = 0$ (excluding infinite temperatures). For $J_2/J_1| < \frac{1}{2}\sqrt{3} = 0.87$ there is one disorder point, for $0.87 < |J_2/J_1| < 0.92$ there are two disorder points, and for $|J_2/J_1| > 0.92$ there are no disorder points. The ground state is ordered for $|J_2/J_1| < 0.5$ and disordered for $|J_2/J_1| > 0.5$. In the upper part of the diagram, the correlations decay in an oscillatory way, whereas in the part below the locus of disorder temperatures, the correlations decay monotonically.

fines a temperature-independent wavelength, and so we have a disorder point of the second kind as defined by Stephenson.[6] Stephenson also defined a temperature T_E at which the relevant correlation, in this case $\langle \frac{3}{2}(\vec{S}_i \cdot \vec{S}_{i+1})^2 - \frac{1}{2}\rangle$, gives zero contribution to the energy $= \langle H \rangle$. It is clear in this simple model that $T_E = T_\Delta$.

In Fig. 6, we show the locus of T_Δ (defined as the temperature at which $R_Q = 0$) as a function of $|J_2/J_1|$. It can be seen that two disorder points can occur only for a very narrow range of values: $0.87 < |J_2/J_1| > 0.92$. At temperatures between these two disorder points the correlations decrease monotonically with distance, whereas at low and high temperatures they decay in an oscillatory manner. The information in Fig. 6 is summarized in Fig. 1, where it can be seen that a single disorder point can occur either with an ordered or a disordered ground state, but two disorder points occur only in the disordered ground-state region.

V. CONCLUSIONS

We have shown that a system of classical spins interacting isotropically with a Heisenberg and a biquadratic exchange between nearest neighbors can be solved exactly in one dimension. This interaction can lead to an eigenvalue degeneracy at $T = 0$ and hence ordering for some values of the parameters. For other values of the parameters there is disorder even at $T = 0$ because of the "packing problem." At finite temperatures, a disorder point may occur when the dipolar and quadrupolar interactions compete. At this temperature the character of the quadrupolar correlations changes from monotonically decreasing to oscillatory. For a small range of parameters two disorder points occur. It is expected that similar behavior may be observed in higher dimensions when competing interactions are present.

After this work was completed, we received preprints of a similar treatment of this problem by Liu and Joseph.[11] They have calculated the eigenvalues of the transition matrix for interactions which are an arbitrary function of $\vec{S}_i \cdot \vec{S}_{i+1}$, but they have not considered the disorder points.

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