Neutron scattering from magnetic polymers

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Some of the static and dynamic properties of a simple magnetic polymer are calculated. The localized magnetic moments on each monomer interact via a nearest-neighbor Heisenberg exchange. While K-independent quantities, like the free energy and the spin-wave density of states are independent of polymer conformation, K-dependent quantities like the wave-vector-dependent susceptibility \(\chi(k)\) and the neutron scattering law \(S(k,\omega)\) can yield useful information about the polymer conformation statistics. Explicit expressions are derived for these quantities for a freely jointed polymer chain. It is shown that the inverse correlation length in a ferromagnetic polymer, which can be determined from \(\chi(k)\), goes as \(k^{-1}\). The neutron scattering law \(S(k,\omega)\) measures essentially the spin-wave density of states at low temperatures although there is some weak \(k\) dependence.

I. INTRODUCTION

One of the main interests in the study of amorphous polymers is to gain information about the conformations of the polymer chains. This can be accomplished in an elastic scattering experiment using, for example, electromagnetic radiation or neutrons. In neutron diffraction, the small-K scattering, which is governed by the neutron scattering length of a monomer, allows the radius of gyration \(R\) of the polymer chain to be determined. The diffraction at larger \(K\) is mainly determined by the internal structure of a single monomer and so does not yield any more information about the polymer conformation. Similar considerations apply in the scattering of x rays and light.

Recent work\(^2\) on the static susceptibility of magnetic polymers has suggested to us the possibility of gaining information about the polymer conformations by performing both elastic and inelastic neutron scattering experiments. The magnetic moments provide convenient “markers” on each monomer and there is no internal molecular structure to complicate the interpretation of the experimental results. The magnetic scattering could be separated from the nuclear scattering by using polarized neutrons if necessary.

It is not unreasonable to expect that the \(K\)-independent magnetic properties of a polymer chain will be independent of the conformation. This will happen, for example, in the polymer shown in Fig. 1 where the spins are located at the ends of each identical monomer and the exchange interactions only couple nearest neighbors. We assume that the polymer is in a dilute solution so that cross linkages and interactions between polymer chains can be neglected. This system is described by the Hamiltonian

\[
H = -J \sum_i \vec{S}_i \cdot \vec{S}_{i+1},
\]  

where \(i\) is an index that labels the spins along the topologically linear polymer chain. The exchange interaction \(J\) will depend upon direct and super-exchange mechanisms within a single monomer and so it will be constant. Of course, more complex magnetic polymers can be imagined in which, for example, the spins are at the center of each monomer and then it would be unreasonable to suppose the exchange interaction to be independent of the angle between adjacent monomers. We shall not consider such complications in this paper.

Some of the static and dynamic properties of the Hamiltonian [Eq. (1)] can be calculated exactly and we will concentrate on these. The static properties of Eq. (1) can be calculated for classical spins.\(^3\) We briefly review this in Sec. II and in Sec. III we calculate \(\chi(k)\) for a freely jointed chain whose properties are also briefly reviewed. The Hamiltonian [Eq. (1)] may be thought of as having a phase transition at zero temperature. Of course the weak magnetic interactions between neighboring polymer chains will lead to a nonzero but very small transition temperature in

![Magnetic polymer](https://via.placeholder.com/150)

**Fig. 1.** Magnetic polymer. Spins are shown by arrows and the monomers are freely jointed.
practice. The neutrons couple to the ordering susceptibility \( \chi(\mathbf{k}) \) as \( \mathbf{K} \to 0 \) in a ferromagnetic polymer. While the inverse correlation length \( 1/\xi \to T \) when measured along the chain, we show that it goes as \( T^{1/2} \) when measured along the direct path. Thus neutrons see an inverse correlation length going as \( T^{1/2} \). When the correlation length becomes comparable to the length of the polymer chain, information can be extracted about the length of the chains. In the antiferromagnet, the neutrons do not couple to the ordering susceptibility and our results show that much less information about the polymer lengths can be extracted.

At low temperatures, the excitations of the system are spin waves. Spin-wave theory for both the ferromagnet and antiferromagnet are briefly reviewed and \( S(\mathbf{k}, \omega) \) is calculated for both cases. The result is rather insensitive to \( k \) and reflects essentially the density of states.

Throughout this work we use the model of a freely jointed polymer chain. This is to make the algebra simple and the use of a more complex model would not alter substantially any of our general results as stated in the conclusion.

II. STATIC PROPERTIES OF CLASSICAL HEISENBERG CHAIN

The thermodynamic properties of the Hamiltonian [Eq. (1)] are the same as for a geometrically linear chain. We will refer to the disordered polymer chain as \textit{topologically linear}. Although the thermodynamic properties of this Hamiltonian are not known analytically for a general spin, they are known in the classical limit (\( S \to \infty, \ h = 0 \), and \( h^2 = 1 \)). The classical result for \( \chi(k) \) has been shown to describe well the antiferromagnetic Mn\(^{1+} \) (\( S = \frac{3}{2} \)) chains in Cd\(_{3}\)NeuCl\(_{3}\) (TMNMC).²

The spins \( \mathbf{S}_i \) become unit classical vectors and the partition function may be written

\[
Z = \int \cdots \int \frac{d\mathbf{S}_i \cdots d\mathbf{S}_N}{(4\pi)^N} e^{-\beta H_{\text{cl}}} = \int \cdots \int \frac{d\mathbf{S}_i \cdots d\mathbf{S}_N}{(4\pi)^N} e^{-\beta H_{\text{cl}}} = \int \cdots \int \frac{d\mathbf{S}_i \cdots d\mathbf{S}_N}{(4\pi)^N} e^{-\beta H_{\text{cl}}},
\]

(2)

where

\[
e^{-\beta H_{\text{cl}}} = e^{2\beta \mathbf{S}_i \cdot \mathbf{S}_j} = 4\pi \sum_{\lambda} \lambda_\lambda(\beta J) Y_{\lambda \lambda}^* (S_i) Y_{\lambda \lambda} (S_j)
\]

(3)

and

\[
\lambda_\lambda(\beta J) = \frac{1}{2} \int_{-1}^{1} e^{2\beta J x} P_\lambda(x) dx.
\]

(4)

The \( Y_{\lambda \lambda} (S_i) \) are the usual spherical harmonics and the \( P_\lambda(x) \) are Legendre polynomials. We assume that both ends of the chain are free and the chain has \( N \) bonds and \( N+1 \) atoms. Using the orthogonality properties of the spherical harmonics, it is easy to see that

\[
\lambda_\lambda(\beta J) = \left[ \lambda_\lambda(\beta J) \right]^*,
\]

(5)

Only the \( l = 0 \) terms are retained because of the integration over the spin variable at the end of the chain, so that the free energy of the chain is given by

\[
F = -k_B T N \ln \lambda_0(\beta J),
\]

(6)

where from Eq. (4)

\[
\lambda_0(\beta J) = (\sinh \beta J) / \beta J.
\]

(7)

The wave-vector-dependent susceptibility for the geometrically linear chain may be written

\[
S(q) = \frac{1}{(N+1)} \sum_{\mathbf{r}} e^{i \mathbf{q} \cdot \mathbf{r}} \langle \mathbf{S}_i \cdot \mathbf{S}_{i+r} \rangle,
\]

(8)

where there is unit spacing between adjacent spins. With a little manipulation, it is easy to show that

\[
\langle \mathbf{S}_i \cdot \mathbf{S}_{i+r} \rangle = \lambda_0(\beta J) \langle \mathbf{S}_i \rangle \langle \mathbf{S}_{i+r} \rangle = \left[ \coth(\beta J) - 1 / \beta J \right] \langle \mathbf{S}_i \rangle^2 = u^2,
\]

(9)

and for an infinite chain (\( N \to \infty \))

\[
S(q) = \sum_{\mathbf{r}} e^{i \mathbf{q} \cdot \mathbf{r}} = \frac{1 - u^2}{1 + u^2 - 2u \cos q}.
\]

(10)

At low temperatures, \( (k_B T / J) \ll 1 \) and small \( q \), \( (q \ll 1) \), which we may call the "critical region," \( S(q) \) has the form

\[
S(q) = \frac{k_B T / J}{(k_B T / J)^2 + q^2},
\]

(11)

so that in this region the correlation length \( \xi_L \) is given by

\[
1 / \xi_L = k_B T / J.
\]

(12)

We see that the correlation length diverges as \( T \to 0 \) as we would expect at a phase transition. The correlation function in Eq. (9) decays exponentially along the chain. This is also true for a polymer chain. However, neutron diffraction experiments measure \( \chi(\mathbf{k}) \) where \( \mathbf{k} \) is a vector in the real space of the polymer. At zero wave vector we have \( \chi(0) = S(0) \), but for a general \( \mathbf{k} \) the situation is more complex and we must know more about the polymer conformation in order to calculate \( \chi(\mathbf{k}) \).

The susceptibility \( S(q) \) for the antiferromagnet is obtained from Eq. (10) by letting \( J \to -J \), i.e., replacing \( u \) by \( -u \). This means that the ordering susceptibility is \( S(x) \) and not \( S(0) \) which is nondivergent at low temperatures. Neutrons cannot
couple to the ordering susceptibility in the antiferromagnetic polymer because the nonlinear polymer configurations make it impossible for the neutron phase to alternate in sign from site to site.

III. STATIC SUSCEPTIBILITY OF POLYMER CHAINS

We assume for simplicity that the polymer chain shown in Fig. 1 is freely jointed, that is, each monomer can assume any angle with an adjacent monomer with equal probability. This assumption will greatly facilitate our discussion without substantially altering any of the general conclusions. A brief discussion of the generalization of the result to other polymer conformation statistics is given at the end of this section.

We shall need to evaluate configuration averages of quantities like

$$e^{i\vec{F}_i(\vec{R}_n-\vec{R}_i)}$$

where \(\vec{R}_n\) is a vector from an arbitrary origin to a spin which lies at the meeting of two monomers as shown in Fig. 1. Denoting a configuration average by curly brackets it is easy to see that

$$\langle e^{i\vec{F}_i(\vec{R}_n-\vec{R}_i)} \rangle = \frac{1}{\pi} \int_0^\pi e^{i\theta \sin \theta} d\theta \frac{\sin k a}{ka} = \delta_{n,0},$$

(13)

and moreover

$$\langle e^{i\vec{F}_i(\vec{R}_n-\vec{R}_i)} \rangle = \delta_{n,0}$$

(14)

because this configuration average can be broken up into independent averages of the kind [Eq. (13)].

We define the configuration averaged, wave-vector-dependent susceptibility \(\chi(\vec{k})\) by

$$\chi(\vec{k}) = \frac{1}{N+1} \sum_{i,j} \left\langle e^{i\vec{F}_i(\vec{R}_n-\vec{R}_i)} \right\rangle \left\langle \vec{S}_i \cdot \vec{S}_j \right\rangle,$$

(15)

where the spin-correlation function is given by Eq. (9) and is independent of the polymer configuration. It is this susceptibility that is measured in a neutron diffraction experiment. For an infinite chain, the geometric series [Eq. (15)] is easily summed to give

$$\chi(\vec{k}) = \frac{1 + su}{1 - su}.$$

(16)

We note that \(\chi(\vec{k})\) only depends on the magnitude of \(\vec{k}\) after the configuration average is done as, of course, there are no preferred spatial directions.

It is necessary to perform this average in Eq. (15) before the sum is done; otherwise the sum cannot be evaluated without a detailed knowledge of the individual polymers. The result [Eq. (16)] is shown in Fig. 2 for ferromagnetic and antiferromagnetic polymers at different temperatures. It can be seen that the susceptibility is a function only of \(su = (\sin ka)/(ka)(\cosh \beta J - 1)/\beta J\) so that a change in \(k\) can be accompanied by a change in \(T\) to give the same value of the susceptibility. This is a feature peculiar to our simple model and would not be true of say the freely rotating chain discussed briefly at the end of this section.

The susceptibility for the antiferromagnetic polymer, also shown in Fig. 2, is always finite and indeed achieves a maximum value at \(T = 0, ka/\pi = 1.43\), which gives a susceptibility of \(1.55\). The susceptibility has a peak in this region at all temperatures. It is as close as \(\chi(\vec{k})\) can come to the ordering susceptibility which would require the neutron phase to have alternating sign at each spin.

The ferromagnetic susceptibility \(\chi(\vec{k})\) has a strong peak at \(ka = 0\) and in the "critical region" \((ka \ll 1, k_B T/\Delta \ll 1)\) we may write Eq. (16) as

$$\chi(\vec{k}) = -\frac{12}{(1/\xi_R)^2 + (ka)^2},$$

(17)

where the inverse correlation length \(1/\xi_R\) is given.

FIG. 2. Wave-vector-dependent susceptibility \(\chi(\vec{k})\) from Eq. (16) plotted against \(ka/\pi\) for two temperatures \(k_B T/\Delta = 0.1\) and 1.0 for the ferromagnetic and antiferromagnetic polymers, respectively.
by

\[ 1/\xi_p = (6k_B T/J)^{1/2}. \tag{18} \]

We see that the correlation length \( \xi_p \) is smaller \((\sim T^{-1/2})\) in the polymer chain than the correlation length \( \xi_L \) in an equivalent but geometrically linear chain \((\sim T^{-1})\). This is because the susceptibility \( \chi(\vec{k}) \) measures distances in real space rather than \( S(q) \) which measures them along the chain. This situation is sketched in Fig. 3. This behavior can be understood by the following simple argument. By expanding Eq. (14) in powers of \( k \), we can easily see that

\[ R_{nn}^2 = \left\{ (R_n - R_0)^2 \right\} = a^2. \tag{19} \]

Remembering that \( \xi_L \) and \( \xi_p \) are defined in units of the monomer length, we have \( \xi_p = \xi_L \) and so as \( \xi_L \sim T^{-1} \), we expect \( \xi_p \sim T^{-1/2} \). This simple argument does not give the factor 6 in Eq. (18). By examining the full expressions for \( S(q) \) and \( \chi(\vec{k}) \) [Eqs. (10) and (15)] we find that

\[ \xi_L^2 = \frac{1}{2} \frac{\sum_{n=-\infty}^{\infty} n^2 u^{|n|}}{\sum_{n=-\infty}^{\infty} n^2 u^{|n|}} = \frac{1}{(1-u)^2} \rightarrow \frac{J}{6k_B T} \cdot \tag{20} \]

\[ \xi_p^2 = \frac{1}{6a^2} \frac{\sum_{n=-\infty}^{\infty} R_{nn}^2 u^{|n|}}{\sum_{n=-\infty}^{\infty} u^{|n|}} = \frac{u}{3(1-u^2)} \rightarrow \frac{J}{6k_B T}. \tag{21} \]

These expressions are obtained by making a small wave-vector expansion. Some care has to be taken over the thermodynamic limit; it is simpler for this purpose to consider a long polymer chain that is a circle topologically. The same result could be obtained for a polymer with free ends—however, the limit \( q \rightarrow 0 \) and \( N \rightarrow \infty \) gives more trouble.

The results we have obtained for the ferromagnetic polymer suggest that it would be interesting to reexamine \( \chi(\vec{k}) \) for a finite chain with \( N \) monomers and \( N+1 \) spins. The result of doing the summation in Eq. (15) for a finite chain is (see Ref. 3):

\[ \chi(\vec{k}) = \frac{1+su}{1-su} \frac{2su}{N+1} \frac{1-(su)^{N+1}}{(1-su)^\frac{1}{2}} \tag{22} \]

and is plotted in Fig. 4 for various chain lengths. It can be seen that the results are very sensitive to the chain length in the "critical region" but not outside. This is because the second term in Eq. 22 is negligible for large \( N \) unless \( su \approx 1 \). Outside the "critical region" the results are not sensitive

![FIG. 3. Correlation length for a ferromagnetic polymer. Susceptibility \( S(q) \) measures the correlation length \( \xi_L \) along the chain, whereas \( \chi(\vec{k}) \) measures the correlation length \( \xi_p \) along the straight line.](image1.png)

![FIG. 4. Wave-vector-dependent susceptibility \( \chi(\vec{k}) \) for polymer chains of length 10, 20, 30, and \( \infty \). All results are for \( k_B T/J = 0.1 \).](image2.png)
to the chain length. For the antiferromagnet the results for \( N = 10 \) are quite insensitive to \( N \), as we would expect.

Finally, we comment briefly on the extension of these results to systems with more complex polymer conformation statistics. The result [Eq. (21)] is quite general, although the summations can only be evaluated if \( \{ R_n \} \) is known. However, in the "critical region" when \( \xi_n \gg 1 \), only \( \{ R_n \} \) for large \( n \) is important. For any flexible chain, \( R_n = nb^2 \) for large \( n \), where \( b \) is some length, and so we have the general result

\[
\xi_n^2 = \frac{b^2}{a^2} \frac{J}{6k_B T}.
\]  

(23)

The idea is that any flexible polymer chain can be replaced by a hypothetical freely joined chain with some effective segment length \( b \). Thus most of the results in this paper are more general than just the simple model considered. This result can be expressed in terms of the radius of gyration. For a long flexible chain the radius of gyration \( \{ s \} = nl^2 \) where \( l \) is some length. It can be shown that \( 6l^2 = b^2 \), so that

\[
\xi_n^2 = \frac{l^2}{a^2} \frac{J}{k_B T}.
\]  

(24)

This result is only valid for long (i.e., \( \gg 100 \)) chains. If the conformation statistics of the chain are known, then \( l^2 \) can be calculated. For example, for a freely rotating chain, where adjacent monomers make an angle \( \theta \) with each other, but the dihedral angle is random, it is easy to show that

\[
l^2 = \frac{a^2}{6} \frac{1 - \cos \theta}{1 + \cos \theta}.
\]

Thus for polymers something like polymethylene, where \( \theta \) is the tetrahedral angle, \( \cos \theta = (-1/3) = 109^\circ \), we have \( l^2 = a^2 \).

IV. SPIN DYNAMICS OF POLYMER CHAINS

At low temperatures it is possible to calculate the neutron scattering law \( S(\mathbf{k}, \omega) \) because the low-temperature excitations of the polymer chain are spin waves. The energies and wave functions of these spin waves are dependent only on the topology of the chain. On the other hand, the geometry of the chain determines how the neutrons excite these spin waves. In a geometrically linear chain, neutrons with a particular \( \mathbf{k} \) excite a response only at a single frequency corresponding to spin waves with wave vector \( \mathbf{k} \). In the polymer, however, neutrons with a particular \( \mathbf{k} \) excite spin waves at all frequencies. We calculate \( S(\mathbf{k}, \omega) \) for the Hamiltonian [Eq. (1)] at low temperatures where spin-wave theory should be applicable. This is perhaps surprising as the chain is not magnetically ordered except at \( T = 0 \). However, the order extends over a sufficiently long distance at low temperatures that spin-wave theory works except perhaps for the lowest frequencies. An alternative justification is that an ordered state exists at the lowest temperatures because of the interactions between polymer chains; these interactions are, however, too weak to affect the spin-wave frequencies.

A. Ferromagnetic polymer

We consider the Hamiltonian [Eq. (1)] for quantum-mechanical spins at low temperatures. The scalar spin product can be written in terms of \( S_x \), \( S_y \), and \( S_z \) where \( x \), \( y \), and \( z \) are an external set of axes and \( z \) is the spin ordering direction. Making the Holstein-Primakoff transformation\(^\text{11}\) to Bose operators,

\[
S'_i = S - a_i^\dagger a_i, \quad S'_i = S'_i + i S'_i = (2S - a_i^\dagger a_i)^{1/2} a_i,
\]

(25)

expanding the square roots and retaining only the quadratic terms, we can rewrite the Hamiltonian [Eq. (1)] as

\[
H = J S \sum_i \left( 2a_i^\dagger a_i - a_i^\dagger a_i + a_i a_i^\dagger \right).
\]  

(26)

This approximation is good at low temperatures when \( \langle a_i^\dagger a_i \rangle \ll 2S \) and the angular brackets denote thermal average. The normal modes of Eq. (26) are independent of the chain configuration and given by the unitary transformation to new operators \( a_x \) where

\[
a_x = \frac{1}{\sqrt{N+1}} \sum_i e^{-i \sigma \cdot a_x} a_x,
\]

(27)

so that the Hamiltonian becomes

\[
H = \sum_x \omega_x a_x^\dagger a_x,
\]

(28)

where

\[
\omega_x = 2JS(1 - \cos q).
\]

(29)

Having found the normal modes of the chain, we are in a position to calculate the neutron scattering law \( S(\mathbf{k}, \omega) \) from Fermi's golden rule

\[
S(\mathbf{k}, \omega) = \frac{2\pi}{N+1} \sum_i \left| \langle 1 | \sum_j e^{i \mathbf{F}_j \cdot \mathbf{k}} S_j | 0 \rangle \right|^2 \delta(\omega - \omega_j),
\]

(29)
where \( x \) can be any direction perpendicular to the spin ordering direction. The expression [Eq. (29)] is strictly valid only at zero temperature where \( |0\rangle \) is the fully aligned ground state of the system. The scattering at small finite temperatures can be obtained from \( S(\vec{k}, \omega) \) by inserting the appropriate Bose factors \( n + 1 \) and \( n \) for neutron energy loss and gain, respectively.

Reexpressing Eq. (29) in Bose operators and keeping only the leading terms we have

\[
S(\vec{k}, \omega) = \frac{4\pi S}{(N+1)^2} \sum_{i,j} e^{i\vec{k} \cdot \vec{r}_i - i\vec{k} \cdot \vec{r}_j} e^{-i\epsilon \delta(\omega - \omega)}
\]

Performing the configuration average of \( S(\vec{k}, \omega) \) for the freely joined chain, we obtain

\[
S(\vec{k}, \omega) = \frac{4\pi S}{N+1} \sum_{i,j} \frac{(\text{sinka})^2}{ka} e^{-i\epsilon \delta(\omega - \omega)}
\]

where \( s \) is defined by Eq. (13). Using the result for the spin-wave dispersion [Eq. (28)], we obtain our final result for \( S(\vec{k}, \omega) \)

\[
S(\vec{k}, \omega) = 4S \frac{1 - [(\text{sinka})/ka]^2}{1 - [(\text{sinka})/ka]^2 + [(\text{sinka})/ka]\omega/(JS)}
\]

This is plotted in Fig. 5 as a function of frequency for various \( \vec{k} \) values. It can be seen that the \( k \) dependence is weak and \( S(\vec{k}, \omega) \) looks essentially like the density of spin-wave states for a ferromagnet \( \rho(\omega) \). Indeed, when \( \pi \alpha = \text{integer}, \) or when \( \pi \alpha = \infty \), we have

\[
S(\vec{k}, \omega) = 4S/(4JS \omega - \omega^2)^{1/2} = 4\pi S \rho(\omega) . \tag{33}
\]

The scattering law \( S(\vec{k}, \omega) \) satisfies some simple sum rules. It is rather easy to see directly from Eq. (30) that

\[
\int_0^\infty S(\vec{k}, \omega) d\omega = 4\pi S , \tag{34}
\]

\[
\int_0^\infty S(\vec{k}, \omega) \omega d\omega = 8\pi S^2 J [1 - \langle \text{sinka} \rangle / ka] .
\]

However, it would be misleading to interpret the ratio of these two moments as a quasiparticle energy—the scattering is much too broad. It is possible that in less random polymers—such as the freely rotating chain—that the \( k \) dependence of \( S(\vec{k}, \omega) \) is more pronounced than for the freely jointed chain studied here, which may be regarded as representing the extreme case of polymer disorder.

B. Antiferromagnetic polymer

The calculation of \( S(\vec{k}, \omega) \) for the antiferromagnetic polymer is similar except for the additional complication that it is necessary to introduce separate Bose operators for the up and down sublattices.\(^8\) For the up sublattice

\[
S_i^+ = S - a_i^+ a_i , \quad S_i^+ = S_i^+ + i S_i^+ = (2S - a_i^+ a_i)^{1/2} a_i , \tag{35}
\]

and for the down sublattice

\[
S_i^- = -S + b_{i+1}^+ b_{i+1} , \quad S_i^- = S_i^- + i S_i^+ = b_i^+ (2S - b_{i+1}^+ b_{i+1})^{1/2} , \tag{36}
\]

where \( i \) goes over the \( N \) spins in the up sublattice. The quadratic part of the Hamiltonian [Eq. (1)] (with \( J = -J \)) becomes

\[
H = JS \sum_i (2a_i^+ a_i + 2b_i^+ b_{i+1} + a_i b_{i+1} + a_i^+ b_i + a_i^+ b_i^+ + a_i b_{i+1} + a_i^+ b_i + a_i^+ b_i^+ b_i^+ b_i) . \tag{37}
\]
This Hamiltonian can be diagonalized by first going to plane-wave operators

\[ a_q = \frac{1}{\sqrt{N}} \sum_r e^{iqr} a_r, \quad b_q = \frac{1}{\sqrt{N}} \sum_r e^{-i(q+r^z)} b_r, \]

and then doing a Bogoliubov transformation to new Bose operators \( \alpha_q \) and \( \beta_q \):

\[ a_q = u_q \alpha_q - v_q \beta_q^\dagger, \quad b_q = u_q \beta_q + v_q \alpha_q. \]

The Hamiltonian becomes

\[ H = \sum_q \omega_q (\alpha_q^\dagger \alpha_q + \beta_q^\dagger \beta_q + 1), \]

where the spin-wave energies are

\[ \omega_q = 2JS \left| \sin q \right| \]

and the real quantities \( u_q \) and \( v_q \) are given by

\[ u_q^2 - v_q^2 = 1, \quad u_q^2 + v_q^2 = \csc q. \]

The neutron scattering law \( \left[ \text{Eq. (29)} \right] \) (with the total number of atoms \( N+1 \) replaced by \( 2N \)) can be written in terms of the Bose operators and becomes

\[ S(\vec{k}, \omega) = \frac{2\pi S}{N^2} \sum_q \left| \langle q \rangle \sum_i \alpha_i^\dagger \{ u_q e^{-i \omega l_{i+1}} e^{i \cdot \vec{k} \cdot \vec{r}_{i+1}} + v_q e^{i \omega l_{i+1}} e^{i \cdot \vec{k} \cdot \vec{r}_i} \} \right|^2 \delta(\omega - \omega_q). \]

Writing the square out explicitly and doing the configurational average for the freely jointed chain we arrive at the final result

\[ S(\vec{k}, \omega) = 4S \left[ 1 - \left( \frac{\sin \omega}{\omega} \right)^2 \right] \left[ 1 - \left( \frac{\sin \omega}{\omega} \right)^2 \right] \frac{\sin \omega}{\omega} \left( \frac{\omega}{J S} \right) \left( \frac{\omega(\omega)}{JS^2} \right) \]

\[ \times 2J S \left( 1 - \frac{\sin \omega}{\omega} \right) + \frac{\omega^2 (\sin \omega / \omega)}{2JS} \] \[ \frac{1}{\omega(2JS)^2 - \omega^2} \] \[ \frac{1}{\omega(2JS)^2 - \omega^2} \]

This is plotted in Fig. 6. The same comments about \( \vec{k} \) selection that we made for the ferromagnet also apply here. For \( \omega / \pi \) integer or \( \omega / \pi = \infty \), we have

\[ S(\vec{k}, \omega) = \frac{4S \omega}{\omega(2JS)^2 - \omega^2} \frac{1}{\omega(2JS)^2 - \omega^2} \frac{\rho_0(\omega)}{\omega} 2JS, \]

where \( \rho_0(\omega) \) is the antiferromagnetic density of states. Note that \( S(\vec{k}, \omega) \) diverges at small \( \omega \) and is nonintegrable. This also happens for a geometrically linear chain at a magnetic reciprocal-lattice point. [The cross section in this case goes as \( \Sigma_q | \tan 3q | \delta(\omega - \omega_q) \).]

V. CONCLUSIONS

We have shown how the wave-vector susceptibility \( \chi(\vec{k}) \) and the neutron scattering law \( S(\vec{k}, \omega) \) may be calculated for a simple magnetic polymer. Our main conclusions are (a) the ferromagnetic susceptibility diverges in the "critical region" with an inverse correlation length going as \( T_1/2 \) and is sensitive to the length of the chain. (b) The antiferromagnetic susceptibility is nonordering and therefore finite and insensitive to the length of the chain. (c) The neutron scattering law \( S(\vec{k}, \omega) \) is only weakly \( \vec{k} \) dependent and looks like the density of spin-wave states at low temperatures.
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5The notation follows that of M. F. Thorpe and M. Blume [Phys. Rev. B **5**, 1961 (1972)].

6W. Kuhn, Kolloid-Z. **76**, 258 (1936); **87**, 3 (1939).
