Thermodynamics of dilute XY quantum chains

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It is shown that the specific heat and susceptibility \( \chi_{\text{sp}} \) of the dilute XY spin-\( \frac{1}{2} \) chain can be calculated by summing over the finite segments. At low temperatures the specific heat is determined by segments with an even number of spins, whereas the susceptibility is determined by segments with an odd number of spins. At low temperatures the specific heat behaves as \( (T_0/T)^{5/4} \exp[-2(T_0/T)^{1/2}] \), where \( T_0 \) is a characteristic temperature in the dilute spin system.

I. INTRODUCTION

In this paper, we show that the thermodynamic properties of the dilute XY spin-\( \frac{1}{2} \) chain can be calculated by evaluating the free energy for finite segments and summing over the various segments with the correct weighting factors. These summations can be performed numerically for chain segments of length up to 500 so that essentially exact results are obtained.

It is shown that the low-temperature behavior of the specific heat is determined by segments with an even number of spins. In particular, the specific heat behaves as \( (T_0/T)^{5/4} \exp[-2(T_0/T)^{1/2}] \) at low temperatures, where \( T_0 \) is a characteristic temperature of the dilute spin system. The derivation of this result closely parallels the derivation of Mott's variable range hopping formula and shows that the specific heat is dominated by a certain range of lengths for segments with an even number of spins. This range depends sensitively on the temperature. On the other hand, the low-temperature behavior of the susceptibility \( \chi_{\text{sp}} \) is determined by the Kramer's degeneracy associated with segments with an odd number of spins.

For small concentrations of nonmagnetic sites, an exact result is derived for the specific heat, and susceptibility \( \chi_{\text{sp}} \) using a rather novel theorem that is proved in the Appendix.

In the remainder of this introduction, the Jordan-Wigner transformation is reviewed for a single finite chain segment. In Sec. II the thermodynamics of a single segment is studied and in Sec. III general expressions are given for the thermodynamic properties of dilute chains, obtained by summing over segments with the correct weighting factors. In Sec. IV the specific heat is examined in detail, and in Sec. V the susceptibility \( \chi_{\text{sp}} \) is discussed. Finally, in the conclusions, the possibility of doing an experiment is explored.

The Hamiltonian for a single segment with \( r \) atoms is given by

\[
H = J \sum_{i=1}^{r-1} (S_i^x S_{i+1}^x + S_i^y S_{i+1}^y) + g \mu_B H \sum_{i=1}^{r} S_i^z .
\]  

(1)

This Hamiltonian has been solved\(^3\,^4\) by first transforming to raising and lowering operators

\[
a_i^\dagger = S_i^+ + i S_i^y, \quad a_i = S_i^- - i S_i^y
\]

(2)

so that the Pauli spin operators are

\[
S_i^x = (a_i^\dagger + a_i)/2, \quad S_i^y = (a_i^\dagger - a_i)/2i,
\]

\[
S_i^z = a_i^\dagger a_i - \frac{1}{2}
\]

(3)

The Hamiltonian becomes

\[
H = \frac{J}{2} \sum_{i=1}^{r-1} (a_i^\dagger a_{i+1} + a_{i+1}^\dagger a_i) + \frac{h}{2} \sum_{i=1}^{r} (a_i^\dagger a_i - \frac{1}{2}) .
\]

where \( h = 2g \mu_B H \).

These operators are not easy to work with as they behave like Fermi operators on the same site

\[
[a_i, a_i^\dagger] = 1; \quad a_i^2 = (a_i^\dagger)^2 = 0
\]

(5)

but like Bose operators on different sites

\[
[a_i^\dagger, a_j] = [a_i^\dagger, a_j^\dagger] = [a_i, a_j] = 0
\]

(6)

However the Jordan-Wigner transformation\(^2\) allows the Hamiltonian to be written entirely in terms of Fermi operators

\[
c_i = \exp \left[ \sum_{j=1}^{i-1} a_j^\dagger a_j \right] a_i
\]

(7)

\[
c_i^\dagger = a_i^\dagger \exp \left[ - \sum_{j=1}^{i-1} a_j^\dagger a_j \right]
\]

Then

\[
c_i^\dagger c_i = a_i^\dagger a_i
\]

(8)
and the inverse transformation is

\[ a_i = \exp \left( -\frac{\pi i}{\hbar} \sum_{j=1}^{r} c_j^+ c_j \right) c_i , \]

\[ a_i^+ = c_i^+ \exp \left( \frac{\pi i}{\hbar} \sum_{j=1}^{r} c_j^+ c_j \right) . \]  (9)

The new operators obey Fermi commutation relations

\[ [c_i, c_j^+] = \delta_{ij} \quad [c_i, c_j] = [c_i^+, c_j^+] = 0 . \]  (10)

We note that

\[ a_i^+ a_{i+1} = c_{i-1}^+ c_i , \]  (11)

so that the Hamiltonian (4) can be rewritten using (8) and (11) as

\[ H = \frac{J}{2} \sum_{i=1}^{r-1} (c_i^+ c_{i+1} + c_{i+1}^+ c_i) + \frac{\hbar}{2} \sum_{i=1}^{r} (c_i^+ c_i - \frac{1}{2}) . \]  (12)

It is convenient to rewrite it as

\[ H = \sum_{j=1}^{r} \sum_{i=1}^{r} c_i^+ c_j A_{ij} c_j - \frac{\hbar r}{4} , \]  (13)

where the matrix \( A \) may be written

\[ A = \frac{1}{2} \begin{bmatrix} h & J & 0 & 0 \\ J & h & 0 & 0 \\ 0 & J & h & 0 \\ 0 & 0 & J & h \end{bmatrix} . \]  (14)

The eigenvalues \( \epsilon \) of \( A \) can be found by writing out the equations for the components of \( v_j \) of an eigenvector \( \nabla \) such that

\[ \epsilon \nabla = A \nabla \]  (15)

that is

\[ 2\epsilon v_1 = h v_1 + J v_2 , \]
\[ 2\epsilon v_2 = h v_2 + J (v_1 + v_3) , \]
\[ \vdots \]
\[ 2\epsilon v_{r-1} = h v_{r-1} + J (v_{r-2} + v_r) , \]
\[ 2\epsilon v_r = h v_r + J v_{r-1} . \]  (16)

This set of equations (excluding the first and last) may be solved by putting

\[ v_s = ve^{ik} , \]  (17)

where

\[ s = 1, 2, \ldots, r \]

so that

\[ \epsilon_r = \frac{h}{2} + J \cos k . \]  (18)

Because solutions with \( \pm k \) are degenerate, the solution to the complete set of equations (including the first and last) can be formed by putting

\[ v_s = \alpha e^{ik} + \beta e^{-ik} . \]  (19)

A little algebra will convince the reader that the first and last equations of (16) are solved if

\[ \beta/\alpha = -1 = -\exp[2(r+1)\imath k] \]  (20)

so that

\[ v_s = 2i \alpha \sin k \]  (21)

where

\[ k = \frac{p \pi}{r+1} ; \quad p = 1, 2, \ldots, r \]  (22)

As expected, the solutions are standing waves rather than the Bloch-type running waves obtained for the cyclical chain. The allowed values of \( k \) are given in Eq. (22). We note that for the anisotropic XY model where the coefficient of \( J/SJ_{n+1} \) is different from the coefficient of \( J/SJ_{n+1} \), an implicit equation is obtained for the allowed values of \( k \). This would make it much more difficult to obtain a solution for the dilute chain.

Kramers theorem states that for systems with an odd number of electrons (\( r \) odd) and the time reversal invariance (\( h = 0 \)) the energy levels should all have an even-fold degeneracy. The energy \( E = \sum_n \varepsilon_n \omega_n \) is the total energy of the system where \( \varepsilon_n = 0 \) or 1. For odd \( r \), there is always a solution with \( k = \pi/2 \) and \( \omega = 0 \) so that every energy \( E \) is at least twofold degenerate because \( \varepsilon_n \varepsilon_k = 0 \) or 1 leads to the same \( E \). We will see that this degeneracy has a profound effect on the results. A little thought will convince the reader that the ground state is never more than twofold degenerate.

**II. THERMODYNAMICS OF A SINGLE SEGMENT**

The partition function can be obtained by noting that the Hamiltonian is now in the form

\[ H = \sum_{k} \left\{ \epsilon_k c_k^+ c_k - \frac{h}{4} \right\} , \]  (23)

where \( \epsilon_k \) is given by (18) and the allowed values of \( k \) for an \( r \) spin segment by (22). The \( c_k \) are normal mode Fermi operators with commutation rules like (10).

The free energy \( F_r \) for the \( r \) spin segment is given by

\[ -\beta F_r = \sum_k \ln[\cosh(\beta \epsilon_k/2)] \]

\[ -\sum_k \ln 2 \cosh(\beta \epsilon_k/2) . \]  (24)
From this we find the internal energy $E$,
\[ E = \frac{\partial (\beta F_r)}{\partial \beta} = -\sum_k \frac{\epsilon_k}{2} \tanh \frac{\beta \epsilon_k}{2} \]  
(25)

and the specific heat $C_r$,
\[ C_r = \frac{\partial E}{\partial T} = k_B \sum_k \left( \frac{\beta \epsilon_k}{2} \tanh \frac{\beta \epsilon_k}{2} \right)^2. \]  
(26)

The magnetization in the negative $z$ direction $M_z$ is given by
\[ M_z = -\frac{\partial F_r}{\partial H} = -2 g \mu_B \frac{\partial F_r}{\partial h} = g \mu_B \sum_k \tanh \frac{\beta \epsilon_k}{2} \]  
(27)

and the susceptibility $\chi^z$ is then
\[ \chi^z = \frac{\partial M_z}{\partial H} = 2 g \mu_B \frac{\partial M_z}{\partial h} = \beta \left( \sum_k \tanh \frac{\beta \epsilon_k}{2} \right)^2. \]  
(28)

Of particular interest to us are the specific heat and susceptibility in zero external field ($h = 0$) given by
\[ C_r = k_B \sum_k \left( \frac{\beta J \cos k}{2} \right)^2 \text{sech} \frac{\beta J \cos k}{2} \right)^2. \]  
(29)
\[ \chi^z = \beta \left( \sum_k \tanh \frac{\beta J \cos k}{2} \right)^2. \]  
(30)

We note that the summation over $k$ goes over the $r$ discrete values given by (22).

\[ \frac{C}{Nk_B} = (1 - c)^2 \frac{\beta J}{2} \cos \frac{p \pi}{r+1} \text{sech} \left( \frac{\beta J}{2} \cos \frac{p \pi}{r+1} \right)^2 \]  
(33)

and the susceptibility $\chi^z$ is
\[ \frac{\chi^z}{N(\frac{1}{2} g \mu_B)^2} = \beta (1 - c)^2 \frac{\beta J}{2} \cos \frac{p \pi}{r+1} \text{sech} \left( \frac{\beta J}{2} \cos \frac{p \pi}{r+1} \right)^2. \]  
(34)

Those double summations can be done numerically. In order to get sufficient accuracy, it was necessary to sum over segments of length up to $r = 500$ for $c = 0.95$. For $c = 1$ only the $r = N$ term is retained in the second summation in (33) and (34). For smaller values of $c$ the series converged much more quickly. The results are therefore exact numerically and are shown in Figs. 2–7. We note that less than 100 s of computer time are needed to evaluate (33) and (34) and these results can be reproduced as required to compare with experimental results. Any desired accuracy can be achieved by extending the summations to larger and larger segments. This only causes difficulty when $c$ is very close to 1. The results (33) and (34) are independent of the sign of $J$.

**III. THERMODYNAMICS OF THE DILUTE CHAIN**

A linear chain with $N \to \infty$ sites can be diluted by removing a fraction $(1 - c)$ of magnetic sites chosen at random. If two adjacent sites are occupied by magnetic ions, then they interact with the $XY$ part of the Hamiltonian (1). Every magnetic site experiences an external field in the $z$ direction as given in (1). It is possible to break up the chain into segments as shown in Fig. 1. The probability $P_r$ of finding a segment with $r$ spins is given by
\[ P_r = N(1 - c)^2 c^r \]  
(31)

so that any thermodynamic quantity of interest $T$ may be written as a summation over the corresponding property for an $r$ spin segment $T_r$,
\[ T = \sum_r P_r T_r. \]  
(32)

The specific heat $C$ is given by

\[ C = (1 - c)^2 \left( \sum_{r=1}^{N} \frac{\beta J}{2} \cos \frac{p \pi}{r+1} \text{sech} \left( \frac{\beta J}{2} \cos \frac{p \pi}{r+1} \right)^2 \right) \]  
(33)

and the susceptibility $\chi^z$ is
\[ \chi^z = \beta (1 - c)^2 \left( \sum_{r=1}^{N} \frac{\beta J}{2} \cos \frac{p \pi}{r+1} \text{sech} \left( \frac{\beta J}{2} \cos \frac{p \pi}{r+1} \right)^2 \right) \]  
(34)

**IV. SPECIFIC HEAT**

The specific heat per magnetic site $C/Nk_B$ is shown in Fig. 2. It is useful to calculate the total en
entropy by integrating this expression. Naively we
would expect this to give a contribution ln2 for each
magnetic spin. However, every segment with an odd
number of spins \((r = 1, 3, 5, \ldots)\) has one zero fre-
cquency excitation because of the Kramers degener-
cy. This leads to a delta function in the specific heat
at zero temperature that is excluded from the integra-
tion. The total number of states involved is
\[
N (1 - c)^2 (c + c^3 + c^5 + \cdots) = \frac{Nc (1 - c)}{1 + c}
\]
so that
\[
\int_0^\infty \frac{C}{k_B T} dT = \left[ Nc - \frac{Nc (1 - c)}{1 + c} \right] \ln 2 ,
\]
\[
\int_0^\infty \left[ \frac{C}{Nc k_B T} \right] dT = \left[ \frac{2c}{1 + c} \right] \ln 2 .
\]
Thus the "entropy integral" for Fig. 2 leads to
\[(2c/(1 + c)) \ln 2\] and for Fig. 3 leads to \[2/(1 + c)\] \times \ln 2. Of course implied in (37) is that the delta
function at \(T = 0\) is excluded from the integration.

Expanding (33) at high temperatures, we obtain
\[
\frac{C}{Nc k_B} = (\beta J)^2 / 8 - (\beta J)^4 (1 + 2c) / 128
\]
\[+ (\beta J)^6 (1 + 6c + 3c^2) / 3072 + \cdots .
\]
At low temperatures for \(c = 1\), we have
\[
\frac{C}{Nk_B} = \frac{\pi}{3} (k_B T/J)
\]
because there is no gap in the excitation spectrum.
When the chain is diluted, gaps occur in the excita-
tion spectrum because of the discrete nature of the
allowed \(k\) states. This leads to an exponentially small
specific heat at low temperatures as is particularly
apparent in the insert in Fig. 3.

We have shown the specific heat/magnetic bond in
Fig. 3 because for many soluble models this is inde-
dependent of \(c\). This happens in the dilute classical
Heisenberg model and the dilute \(S = 1/2\) Ising model
where the bonds essentially behave independently.\(^6\)
This is clearly not the case here.

Further analysis at very low temperatures shows that
the specific heat of a single segment behaves as
\[
C/k_B = \frac{1}{2} (\beta \Delta E)^2 \exp (-1/2 \beta \Delta E)
\]
for \(k_B T < \Delta E\) where \(\Delta E = J \pi/(r + 1)\) for even
chains and \(\Delta E = 2J \pi/(r + 1)\) for odd chains. This is
obtained by taking just the lowest-energy excitation
between the discrete levels. The difference occurs
because the odd segments have a state exactly at the
Fermi level that does not contribute to the total en-
ergy, whereas the even segments do not. The contri-
bution from the odd chains is insignificant and we
may write the specific heat for the dilute system as
\[
C/Nk_B = x^2 \sum_{i=1}^{N_c} \left( \frac{1}{2} (\beta J \pi)/(r + 1) \right)^2 \times \exp \left( -1/2 (\beta J \pi)/(r + 1) \right)
\]
where $x = 1 - c$ and the prime on the summation denotes even $r$ only. If $x$ is small so that the segments are large on average, the summation can be converted into an integral

$$C/Nk_B = (T_0/T)^2 \int_0^\infty \exp\{-rx - 2 \ln r - T_0/(rxT)\} dr \; , \quad (42)$$

where

$$k_B T_0 = \frac{1}{2} J \pi x \; . \quad (43)$$

This integral can be evaluated by the method of steepest descents. The term $-T_0/(rxT)$ dominates at small $r$, and the term $-rx$ at large $r$. The $-2lnr$ plays no significant role and may be taken outside the integral and replaced by $1/r\hat{r}$ where $r_0$ is the value of $r$ at the saddle point given by

$$r_0 = \frac{1}{x} \sqrt{T_0/T} \; . \quad (44)$$

Physically this means that there is a trade off between large segments that produce small energy gaps and small segments that occur with higher probability. The specific heat is dominated by segments of intermediate length that represent a compromise between these two desirable characteristics.

We may write

$$\frac{C}{Nk_B} = \left\{ \frac{T_0}{T} \right\}^2 \frac{1}{r\hat{r}} \int_{-\infty}^{\infty} e^{-\alpha(r-r_0)^2} e^{-2(r/r\hat{r})^{1/2}} dr \; , \quad (45)$$

where

$$\alpha = x^2(T/T_0)^{1/2} \; . \quad (46)$$

The method is valid if

$$\sqrt{\alpha r_0} >> 1 \; , \quad (47)$$

i.e.,

$$(T_0/T)^{1/4} >> 1 \quad (47)$$

and then

$$C/Nk_B = x \sqrt{\pi} (T_0/T)^{3/4} \exp\{-2(T_0/T)^{1/2}\} \; . \quad (48)$$

This result and argument are very similar to Mott's variable range hopping where the segment length plays the role of the hopping range. It only works at temperatures much lower than $T_0$ as shown by the condition (47). This result has been checked against the computer results as shown in Fig. 4. We note that for $c = 0.90$ and 0.95, $k_B T_0/J = 0.157$ and 0.079, respectively. The crossover from approximately linear to exponential behavior occurs at around $T_0/10$. In this region the specific heat is dominated by segments of length $r_0 \pm \alpha^{-1/2}$. For example, for $c = 0.90$ and $T = T_0/20$, this leads to dominant segment lengths of $45 \pm 21$.

Finally we use the thermodynamic perturbation theory in the Appendix for small $x = 1 - c$. In Fig. 5, the exact analytic result and the computer results for the specific heat are compared for $c = 0.90$ and $c = 0.95$. It can be seen that the perturbation theory works well except at very low temperatures where it breaks down for any finite $x$. This is because the perturbation theory is incapable of giving the change over from exponential to power-law behavior.

FIG. 4. A plot of the specific heat at very low temperatures. The solid line is the theory given in the text and the points are from the computer results. The parameter $y = T_0/T = (J \pi x)/(2k_B T)$.

![Graph showing specific heat at low T](image-url)

FIG. 5. Showing the result of perturbation theory (solid line) and the points from the computer results for the specific heat at small $x = 1 - c$. [Graph showing comparison of perturbation theory and computer results]
V. SUSCEPTIBILITY

The susceptibility per magnetic site

\[ \chi_s = \chi^2/[Nc(\frac{1}{2} g \mu_B)^2] \]  \hspace{1cm} (49) 

is shown in Fig. 6. At low temperatures, the behavior is controlled by the degenerate Kramers doublet ground state of the segments with an odd number of spins. The magnetic field in (23) splits the degenerate ground state at \( E_0 \) into two states at \( E_0 \pm h/4 \) in which the magnetization is \( \pm \frac{1}{2} g \mu_B \), respectively. This leads to a Curie susceptibility

\[ \chi = \beta \left( \frac{g \mu_B}{2} \right)^2 \]  \hspace{1cm} (50) 

The susceptibility for those segments with an even number of spins is exponentially small at low temperatures. Therefore summing over all odd segments, we obtain

\[ \chi^2 = \beta \left( \frac{g \mu_B}{2} \right)^2 (1-c)^2(c+c^3+c^5+\cdots) \]

\[ = \beta \left( \frac{g \mu_B}{2} \right)^2 \frac{Nc(1-c)}{1+c} \]  \hspace{1cm} (51)

or

\[ \chi_s = \beta \frac{(1-c)}{(1+c)} \]  \hspace{1cm} (52)

that is shown in the insert in Fig. 6. At zero temperature as \( c \to 1 \) the susceptibility \( \chi_s \to 4/\pi \). At high temperatures from Eq. (34)

\[ k_B T \chi_s = 1 - (\beta J)^2 c/(8 + \beta J)^4 c(1+2c)/192 \]

\[ - (\beta J)^4 17 c(1+6c+3c^2)/92180 + \cdots \]  \hspace{1cm} (53)

In Fig. 7 we make a Curie-type plot of \( 1/\chi_s \) against \( T \). While the slopes are all the same at high temperatures, there is considerable variation at low temperatures. It can be seen from high-temperature series that the Curie-Weiss constant \( \Theta \) defined by \( 1/\chi_s = k_B(T+\Theta) \) is zero for all concentrations as would be expected. The susceptibility \( \chi^2 \) gives no information on the tendency to order within the segments at low temperatures as this takes place within the \( XY \) plane. Unfortunately it does not seem possible to calculate the susceptibility within the plane in any simple way.

For small \( x = 1 - c \), it is possible to do thermodynamic perturbation theory in a similar way to that done for specific heat. This is discussed in the Appendix.

VI. CONCLUSION

We have calculated the specific heat and susceptibility \( \chi^2 \) for dilute \( XY \) chains. The results are independent of the sign of the exchange interaction. This is because there is a symmetry operation, in which \( J \to -J \) and the rotation \( x \to -x, y \to -y, z \to -z \) is performed at every other site, that leaves the Hamiltonian invariant.

![FIG. 6. The susceptibility per magnetic site \( \chi_s \) at low temperatures. The \( c = 0 \) result is for a single isolated spin.](image1)

![FIG. 7. The inverse susceptibility \( 1/\chi_s \) for various values of the concentration \( c \). The \( c = 0 \) result is for a single isolated spin.](image2)
The general technique can be applied to other one-dimensional systems in which the randomness chops the system into noninteracting segments. The only requirement is that the quantity of interest can be calculated for a single finite segment of arbitrary length.

We note that if the dilution is accomplished by removing bonds with probability \((1 - c)\); rather than sites then

\[
cT_b = T_s,
\]

where \(T_b\) is some quantity of interest with a fraction \((1 - c)\) of bonds removed and \(T_s\) is the corresponding quantity of interest in a similar system with a fraction \((1 - c)\) of the sites removed.

Although no experiments measuring the specific heat or susceptibility on systems like this have yet been reported, \(\text{Pr}_3(C_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}\) appears to correspond to an \(XY\) chain (with \(c = 1\)).\(^7\)\(^8\) Dilution can be achieved by substituting Sm ions for Pr ions.\(^9\)

The Sm-Pr interaction is smaller than the Pr-Pr interaction by a factor of about 250. As the Pr-Pr exchange \(J/k_B = 0.76\) K, there should be a region between 10 and 100 mK where the exponential behavior [Eq. (48)] can be seen but where the Pr-Sm interaction is not important. However, the hyperfine interaction becomes important at these low temperatures and the effect will probably be masked.

Note added in proof: The case of an arbitrary distribution of band strengths has been considered by E. R. Smith [J. Phys. C 3, 1419 (1970)]. However, these distributions are smooth and do not contain delta functions. Very different results for the thermodynamics are obtained as the chains do not break up into finite segments.

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APPENDIX

In this Appendix we prove a theorem that is very useful in determining the properties of chains which contain just a few isolated breaks.

Theorem: Given some function \(f_s(k)\) where \(k = p\pi/(r+1)\) and \(p = 1, 2, \ldots, r\) for an \(r\) unit segment, then

\[
\Delta = \lim_{r \to \infty} \left[ \frac{1}{r} \sum_{k} f_s(k) - 2 \sum_{k} f_s(k) \right] = \frac{1}{2} \left[ f(0) + f(\pi) \right] - \frac{1}{2} \left[ f(\pi) + f(\pi/2) \right] - \frac{1}{2} \left[ f(\pi/2) + f(\pi) \right] - \frac{1}{2} \left[ f(\pi) + f(2\pi) \right].
\]

\[\text{(A1)}\]

By taking the limit \(r \to \infty\), we are finding the difference in the quantity \(\sum_{k} f(k)\) for a long chain with and without a single missing site.

Proof: For the two smaller segments \(k_1 = p_1\pi/(r+1)\) with \(p_1 = 1, 2, \ldots, r\) and for the large segment \(k_2 = \frac{1}{2}p_2\pi/(r+1)\). By pairing off various terms in (A1) we may write

\[
\Delta = \lim_{r \to \infty} \left[ f(\pi/2r) + \sum_{k_1} \left[ f(k_1 + \pi/2r) - f(k_1) \right] \right].
\]

\[\text{(A2)}\]

For large \(r\), we may use a Taylor expansion on the second term to give

\[
\Delta = \lim_{r \to \infty} \left[ f\left(\frac{\pi}{2r}\right) + \frac{\pi}{2r} \sum_{k} \frac{\partial f}{\partial k} \right]
\]

\[\text{(A3)}\]

or

\[
\Delta = f(0) + \frac{1}{2} \int_0^\pi \frac{\partial f}{\partial k} dk.
\]

i.e.,

\[
\Delta = \frac{1}{2} \left[ f(0) + f(\pi) \right]
\]

which proves the theorem.

We apply this theorem to the two quantities of interest in this paper; the specific heat and the susceptibility \(\chi^x\). For the specific heat, from Eq. (29) we can identify \(f(k)\) with

\[
f(k) = k_B \left[ \frac{\beta J \cos k}{2} \right] \left[ \frac{1}{\cosh \left( \frac{\beta J \cos k}{2} \right)} \right]^2
\]

so that

\[
\frac{1}{2} \left[ f(0) + f(\pi) \right] = k_B \left[ \frac{\beta J}{2} \right] \left[ \frac{1}{\cosh \left( \frac{\beta J}{2} \right)} \right]^2
\]

\[\text{(A5)}\]

and we may write the specific heat \(C(c)\) as an expansion in powers of \((1 - c)\)

\[
C(c) = C(1) + N(1 - c) \Delta C,
\]

\[\text{(A6)}\]

where

\[
\Delta C = -k_B \left[ \frac{\beta J}{2} \right] \left[ \frac{1}{\cosh \left( \frac{\beta J}{2} \right)} \right]^2
\]

\[\text{(A7)}\]

The assumption made here is that at small \(x = 1 - c\), the defects are spaced far apart and therefore isolated from one another. The comparison with the computer results in Fig. 5, verifies this assumption.

A similar result can be obtained for the susceptibility \(\chi^x(c)\) by using Eq. (30) rather than (29):

\[
\chi^x(c) = \chi^x(1) + N(1 - c) \Delta \chi^x,
\]

\[\text{(A8)}\]

where

\[
\Delta \chi^x = -\beta \left[ \frac{g\mu_B}{2} \right]^2 \left( \frac{1}{\cosh \left( \frac{\beta J}{2} \right)} \right)^2
\]

\[\text{(A9)}\]
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