Effect of a magnetic field on the thermodynamics of dilute XY quantum chains

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We investigate the effect of a magnetic field along the z direction on the magnetization, longitudinal susceptibility, and specific heat of the dilute XY quantum chain. The introduction of the field emphasizes the effect of the strong discretization of the modes giving rise to anomalies in the field dependence of the thermodynamic properties which should be experimentally observable at low temperatures.

I. INTRODUCTION

The XY model of a linear chain of spin $\frac{1}{2}$, first studied by Lieb, Schultz, and Mattis[1] and Katsura,[2] is of great interest because many properties can be calculated exactly. In fact, using the well-known Jordan-Wigner transformation, the XY spin Hamiltonian is mapped onto a simple free-fermion system. In the presence of a magnetic field along the z axis the static and dynamic properties have also been exactly calculated by Niemeijer.[3] For fixed $T=0$ he found a divergent behavior for the longitudinal magnetic susceptibility χ^{zz} indicating a second-order phase transition in the neighborhood of a critical field.

Since the Hamiltonian of the XY model is exactly diagonalized even in the case of a segment with any number of spins, exact results can be obtained for the physical properties of the dilute system. In a magnetic system, dilution can be achieved by the random substitution of a number of magnetic ions with nonmagnetic ones which divide the chain into noninteracting segments. The physical properties can be calculated summing over the various segments with opportune weighting factors.[4-7] Recently, Thorpe and Miyazima (TM)[4] calculated the thermodynamic properties for the dilute isotropic XY model in zero field. In the low-temperature limit they found that the specific heat is determined by segments with an even number of spins, while the susceptibility is determined by segments with an odd number. The most striking consequence of the dilution appearing from their results is an exponential behavior, near $T=0$, for the specific heat versus temperature.

In this paper we study the effect of a magnetic field along the z direction on the thermodynamics of the dilute XY chain. The introduction of this new parameter leads to a more marked dependence of the physical properties on dilution, giving rise to anomalies which should be easily detectable in real systems. At $T=0$, varying the field the magnetization presents an infinite number of steps, a feature earlier reported by Matsubara and Katsura,[7] signaling the coming into play of each single mode. For the specific heat and the susceptibility we find peaked structures. At very low but finite temperatures, these anomalies are smoothed but should be still experimentally observable.

II. THERMODYNAMIC PROPERTIES

The XY Hamiltonian for a single segment with j atoms is given by

$$\mathcal{H}=J\sum_{i=1}^{j-1}(S_i^xS_{i+1}^x+S_i^yS_{i+1}^y)+g\mu_BH\sum_{i=1}^{j}S_i^z\ . \tag{1}$$

Following TM (Ref. 4) (to whom we refer for details) this Hamiltonian is diagonalized in terms of fermion operators using the Jordan-Wigner transformation:

$$\mathcal{H}=\sum_k(\epsilon_k c_k^\dagger c_k-h/4)\ , \tag{2}$$

where $h=2g\mu_BH$; $c_k^\dagger$ and c_k are Fermi creation and annihilation operators, respectively. The Fermi excitations have the dispersion relation

$$\epsilon_k=J\cos k+h/2 \tag{3}$$

with

$$k=p\pi/(j+1),\quad p=1,2,\ldots,j\ . \tag{4}$$

From the free energy for the j-spin chain:

$$F_j=-\beta^{-1}\sum_k\ln[2\cosh(\beta\epsilon_k/2)] \tag{5}$$

any thermodynamic property can be derived. For the magnetization:

$$M_j^z=-\frac{\partial F_j}{\partial H}=\frac{g\mu_B}{2}\sum_k\tanh(\beta\epsilon_k/2)\ . \tag{6}$$

For the longitudinal susceptibility:

$$\chi_j^{zz}=\frac{\partial M_j}{\partial H}=\beta\left[\frac{g\mu_B}{2}\right]^2\sum_k\mathrm{sech}^2(\beta\epsilon_k/2) \tag{7}$$

and for the specific heat:

$$C_j=-T\frac{\partial^2F_j}{\partial T^2}=k_B\sum_k[(\beta\epsilon_k/2)\,\mathrm{sech}(\beta\epsilon_k/2)]^2\ . \tag{8}$$

By means of Eqs. (6)—(8) it is possible to evaluate the thermodynamic properties of the dilute chain summing over all the segments weighted by their probability of occurrence: For example, for the magnetization we have[4]

$$M^z=\sum_j P_j M_j^z \tag{9}$$

and analogous expressions for the other thermodynamic properties. The probability P_j of finding a spin segment of length j in a dilute chain with $n\to\infty$ spins is given by[4]

$$P_j=N(1-c)^2c^j\,, \tag{10}$$

where a fraction $(1-c)$ of magnetic sites are randomly removed.

III. RESULTS

We now present the results for the thermodynamic properties obtained in the presence of the field. For the magnetization we have

$$\left[\frac{M^z}{Ng\mu_B}=\frac{(1-c)^2}{2}\sum_{j=1}^{N}c^j\sum_{m=1}^{j}\tanh\left\{\frac{1}{2T^*}\left[\cos\left[\frac{m\pi}{j+1}\right]+\frac{h^*}{2}\right]\right\}\right., \tag{11}$$

where $T^*=k_BT/J$ and $h^*=h/J$. For the pure chain ($c=1$) Niemeijer[3] found for $T\to 0$:

$$\left[\frac{M^z}{Ng\mu_B}\right]_{T\to 0}=\begin{cases}\frac{1}{2}[1-(2/\pi)\cos^{-1}(h^*/2)], & h^*<h_c^* \quad (12a)\\ \frac{1}{2}, & h^*>h_c^* \quad (12b)\end{cases}$$

where $h_c^*=2$ represents the critical value of the field beyond which the energy of the excitations [Eq. (3)] is positive. For the dilute chain we obtain (for details see the Appendix)

$$\left[\frac{M^z}{Ng\mu_B}\right]_{T\to 0}=\begin{cases}(1-c)^2\sum_{j=1}^{N}c^j\,\mathrm{Int}\left[\frac{j+1}{\pi}\cos^{-1}\left[\frac{-h^*}{2}\right]\right]-\frac{c}{2}, & h^*<h_c^* \quad (13a)\\ c/2, & h^*>h_c^* \quad (13b)\end{cases}$$

where Int denotes the integer portion of a number, as found earlier by Matsubara and Katsura.[7]

It can be noted that also for the dilute system the magnetization is saturated for $h^*>h_c^*$. Moreover, it is worthwhile observing that for $h^*<h_c^*$ the magnetization presents a step for each value of the field which satisfies the following relation:

$$\pi^{-1}\cos^{-1}(-h^*/2)=n/(j+1) \tag{14}$$

with $n/(j+1)\in[\frac{1}{2},1)$ and n integer. In Fig. 1 we report

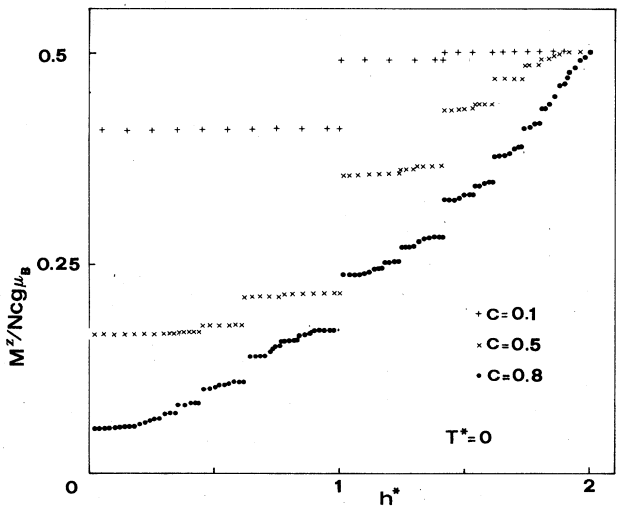

FIG. 1. Reduced magnetization $M^z/Ncg\mu_B$ at $T=0$ versus magnetic field h^* for different concentrations of magnetic sites.

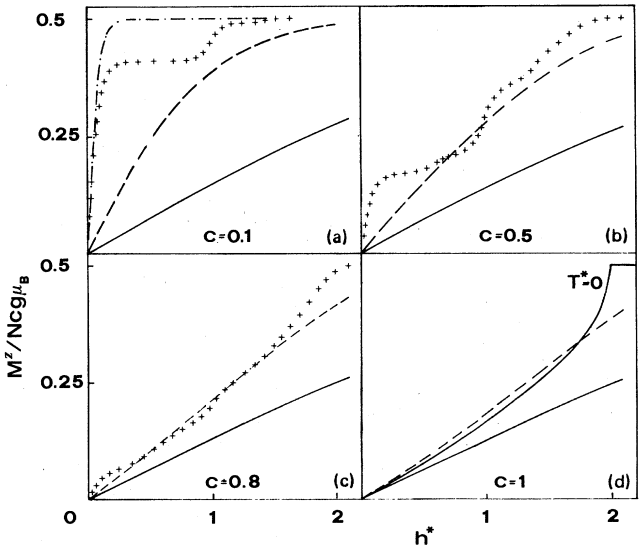

FIG. 2. Field dependence of the reduced magnetization at different concentrations and temperatures. Crosses, $T^*=0.025$; dashed line, $T^*=0.2$; solid line, $T^*=0.8$; dot-dashed line, Brillouin function for $S=\frac{1}{2}$ and $T^*=0.025$.

the magnetization at $T^*=0$ versus h^* for different concentrations of magnetic sites. Such stepwise curves have been earlier reported by Matsubara and Katsura.[7] The limited number of observable steps is only due to scale factors since the contribution from long segments are made irrelevant by the weighting factors c^j.

In Figs. 2(a)–2(d) we report the field dependence of magnetization at different concentrations and temperatures as given by Eq. (11). The effect of the temperature is a smoothing of the steps which are still visible for low temperatures and rapidly disappear at higher temperatures. In Fig. 2(a) we also report the Brillouin function $B_s(g\mu_B HS/k_B T)$ for $S=\frac{1}{2}$ and $T^*=0.025$, which gives the magnetization for a system of noninteracting spins. For low fields this result does not differ substantially from the magnetization of the dilute XY model. This fact can be easily understood since for this low concentration ($c=0.1$) the first step in the magnetization is mainly determined by the contribution of segments with only one spin. The slower saturation of the magnetization for the XY model is due to the presence of longer segments for which there is a competition between the exchange within the XY plane and the Zeeman energy which favors the aligning along the z direction. From Fig. 2(d), which refers to the pure case, it can be noted that there is a range of values of h^* and T^* where the magnetization is greater than at $T^*=0$ for the same value of the field, as already found by Katsura.[2] In Fig. 3 we show the temperature dependence of the reduced magnetization M/c for fixed field at different concentrations. A maximum is present both in the pure and dilute case, indicating that the out-of-plane fluctuations tend to minimize the Zeeman energy. For the dilute chain the peak height is greater and its position shifted to lower temperatures because in this case the polarizing effect of the field is stronger than for the pure system.

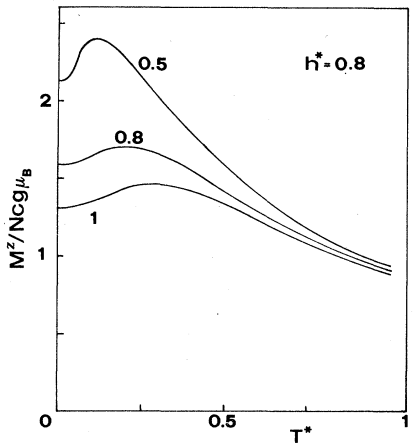

FIG. 3. Temperature dependence of the reduced magnetization for fixed field $h^*=0.8$ at different concentrations.

The peculiar behavior shown by the dilute system when the field is varied can be put in stronger evidence studying a differential property such as the longitudinal susceptibility χ^{zz}. In Fig. 4 we report the field dependence of susceptibility at different concentrations and temperatures given by

$$\frac{J\chi^{zz}}{N(g\mu_B)^2}=\frac{1}{4}\frac{(1-c)^2}{T^*}\sum_{j=1}^{N}c^j\sum_{m=1}^{j}\operatorname{sech}^2\left\{\frac{1}{2T^*}\left[\cos\left[\frac{m\pi}{j+1}\right]+\frac{h^*}{2}\right]\right\}. \tag{15}$$

At low temperatures the main feature is the presence for $h^*<h_c^*$ of several peaks, whose number increases when the concentration of magnetic sites is increased. This fact, which is strictly connected with the steps present in the magnetization, can be better understood referring to the $T=0$ result (see the Appendix):

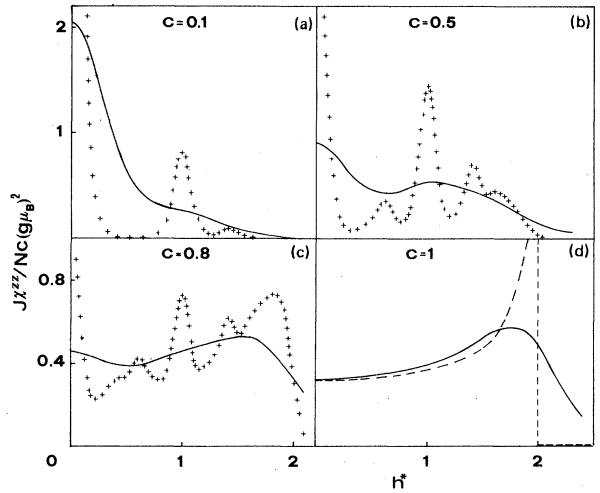

FIG. 4. Field dependence of susceptibility at different concentrations and temperatures. Dashed line, $T^*=0$; crosses, $T^*=0.025$; solid line, $T^*=0.1$.

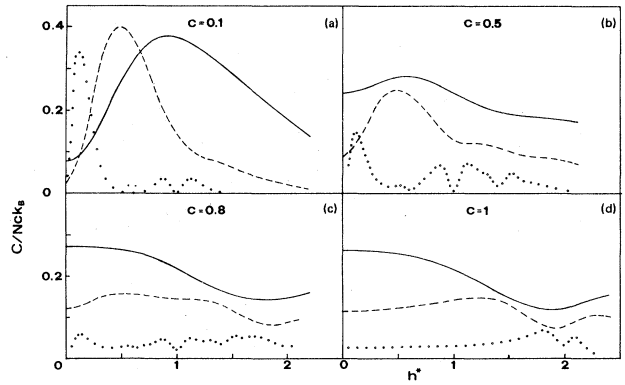

FIG. 5. Field dependence of specific heat at different concentrations and temperatures. Crosses, $T^*=0.025$; dashed line, $T^*=0.1$; solid line, $T^*=0.2$.

$$\frac{J\chi^{zz}}{N(g\mu_B)^2}=\begin{cases}4(1-c)^2\sum_{j=1}^{N}c^j\sum_{m=1}^{j}\delta(h^*-h_m^*), & h^*<h_c^* \quad (16a)\\ 0, & h^*>h_c^* \quad (16b)\end{cases}$$

where

$$h_m^*=-2\cos[m\pi/(j+1)] \quad (17)$$

which reduces to the Niemeijer's result for the pure case.[3] The peaks observed at finite temperatures in Fig. 4 originate from the δ functions present in Eq. (16a). The increasing number of peaks for higher concentrations is simply due to the stronger statistical weight of longer segments which involve the coming into play of new modes.

Now we consider the specific heat, given by

$$\frac{C}{Nk_B}=(1-c)^2\sum_{j=1}^{N}c^j\sum_{m=1}^{j}\left[\frac{1}{2T^*}\left[\cos\left[\frac{m\pi}{j+1}\right]+\frac{h^*}{2}\right]\operatorname{sech}\left\{\frac{1}{2T^*}\left[\cos\left[\frac{m\pi}{j+1}\right]+\frac{h^*}{2}\right]\right\}\right]^2 . \quad (18)$$

Let us begin with the pure system. From Eq. (8) it is seen that the contribution is maximum for

$$\beta\epsilon_k/2=\coth(\beta\epsilon_k/2)\,, \quad (19)$$

i.e., for $(\beta\epsilon_k/2)\sim\pm1.2$. Consequently we have a peak for the field dependence of the specific heat every time the region of the dispersion curve corresponding to the higher density of states ($k\sim\pm\pi$) is lifted in the neighborhood of $\epsilon_k\sim\pm2.4/\beta$. This fact explains the two-peaked structure observed at low temperatures for the specific heat versus h^* for the pure system [Fig. 5(d)]. For the dilute system [Figs. 5(a)–5(c)] we observe a multipeaked structure, due to the fact that in this case, the modes being strongly discretized, the specific heat is sensible to the entrance of a single mode into the aforementioned energy regions.

We remind the reader that in the absence of the field at low temperatures, TM (Ref. 4) found that the specific heat (the longitudinal susceptibility) is determined by segments with an even (odd) number of spins. In the presence of the field, this distinction no longer applies but a complementarity in the results for specific heat and susceptibility is present. In fact, owing to the additional factor $(\beta\epsilon_k/2)^2$ in Eq. (8) with respect to Eq. (7), the positions of the minima in the specific heat nearly coincide with the peak positions for the susceptibility (see Figs. 4 and 5).

IV. CONCLUSIONS

In this paper we have studied the field dependence of the magnetization, the longitudinal susceptibility and the specific heat for the dilute XY quantum chain in the presence of a field applied along the z direction. The introduction of the field turns out to be crucial in order to stress the dependence of the physical properties on dilution with respect to the results of Thorpe and Miyazima[4] for $h=0$. The strong discretization of the modes in the dilute system gives rise to anomalies in the field dependence of the thermodynamic quantities which are more evident the lower the temperature. We suggest that these effects should be experimentally observable, introducing nonmagnetic impurities at random into the compounds $PrCl_3$ (Refs. 8–11) ($J=2.4$ K) and $Pr(C_2H_5SO_4)_3\cdot9H_2O$ (Refs. 12 and 13) ($J=0.76$ K) which are known to be described by the isotropic XY spin $=\frac{1}{2}$ model. Since the most striking effects in the field dependence of thermodynamic properties are present for very low temperatures, $PrCl_3$ is a better candidate for experiments owing to its higher value of the Pr-Pr exchange interaction. Dilution can be obtained introducing nonmagnetic lanthanum (La) impurities.[14,15] The temperature at which the three-dimensional ordering occurs (0.43 K in the pure system) will be strongly lowered by the presence of impurities.[16,17]

APPENDIX

Firstly, we deduce from Eq. (11) the expression at $T=0$ for the magnetization of the dilute XY chain. We distinguish the two cases: $h^*>h_c^*$ and $h^*<h_c^*$. For $h^*>h_c^*$ the argument of $\tanh(\beta\epsilon_k/2)$ in Eq. (11) is always positive; expanding for low temperatures we have

$$\lim_{N\to\infty}\left[\frac{M^z}{Ng\mu_B}\right]_{T^*=0}=\lim_{N\to\infty}\left[\frac{(1-c)^2}{2}\sum_{j=1}^{N}c^jj\right]=\frac{c}{2}\,. \quad (A1)$$

For $h^*<h_c^*$ we observe that, since the energy ϵ_k changes its sign, the m summation must be separated in the following way:

$$\sum_{m=1}^{j}(\cdots)=\sum_{m=1}^{r_j}(\cdots)+\sum_{m=r_j+1}^{j}(\cdots)\,, \quad (A2)$$

where

$$r_j=\operatorname{Int}\left[\frac{j+1}{\pi}\cos^{-1}(-h^*/2)\right]. \quad (A3)$$

Expanding for $T \to 0$ we obtain

$$\left[\frac{M}{Ng\mu_B}\right]_{T=0} = \frac{(1-c)^2}{2}\sum_{j=1}^{N} c^j(2r_j - j)$$
$$= (1-c)^2 \sum_{j=1}^{N} c^j r_j - \frac{c}{2} \quad \text{as } N \to \infty \tag{A4}$$

which coincides with Eq. (13a).

We now perform the limit $T \to 0$ in Eq. (15) for the longitudinal susceptibility. For $h^* > h_c^*$ we find

$$\frac{J\chi^{zz}}{Ng\mu_B)^2} \sim (1-c)^2 \sum_{j=1}^{N} c^j \sum_{m=1}^{j} \frac{1}{T^*} \exp[-\epsilon(m)/T^*] , \tag{A5}$$

where $\epsilon(m) = \cos(m\pi/j+1) + h^*/2$ assumes only positive values and consequently we obtain Eq. (16b). For $h^* < h_c^*$ we have

$$\frac{J\chi^{zz}}{N(g\mu_B)^2} \sim \frac{1}{T^*}(1-c)^2 \sum_{j=1}^{N} c^j \left[\sum_{m=1}^{r_j} \exp[-\epsilon(m)/T^*] + \sum_{m=r_j+1}^{j} \exp[\epsilon(m)/T^*] \right]$$
$$= (1-c)^2 \sum_{j=1}^{N} c^j \sum_{m=1}^{j} \left[\frac{1}{T^*} \exp[-|\epsilon(m)|/T^*] \right] . \tag{A6}$$

We observe that for $T^* \to 0$ the function in large parentheses in Eq. (A6) behaves like $\delta(|\epsilon(m)|)$, i.e., a Dirac δ function. Indicating by

$$h_m^* = -2\cos[m\pi/(j+1)] \tag{A7}$$

the values of the field for which $|\epsilon(m)| = 0$, Eq. (A6) takes the form of Eq. (16a).

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[1]E. Lieb, T. Schultz, and D. Mattis, Ann. Phys. (N.Y.) **16**, 407 (1961).

[2]S. Katsura, Phys. Rev. **127**, 1508 (1962).

[3]Th. Niemeijer, Physica (Utrecht) **36**, 377 (1967).

[4]M. F. Thorpe and S. Miyazima, Phys. Rev. B **24**, 6686 (1981).

[5]A. R. McGurn and M. F. Thorpe, J. Phys. C **16**, 1255 (1983); M. F. Thorpe, A. R. McGurn, and S. Miyazima, *Excitations in Disorder Systems* edited by M. F. Thorpe (Plenum, New York, 1982), p. 601.

[6]M. Thomsen and M. F. Thorpe, J. Phys. C **16**, 4191 (1983).

[7]F. Matsubara and S. Katsura, Prog. Theor. Phys. **49**, 367 (1973).

[8]J. P. Harrison, J. P. Hessler, and D. R. Taylor, Phys. Rev. B **14**, 2979 (1976).

[9]M. Bevis, A. J. Sievers, J. P. Harrison, D. R. Taylor, and D. J. Thouless, Phys. Rev. Lett. **41**, 987 (1978).

[10]M. D'Iorio, R. L. Armstrong, and D. R. Taylor, Phys. Rev. B **27**, 1664 (1983).

[11]E. Goovaerts, H. De Raedt, and D. Schoemaker, Phys. Rev. Lett. **52**, 1649 (1984).

[12]J. T. Folinsbee, J. P. Harrison, D. B. McColl, and D. R. Taylor, J. Phys. C **10**, 743 (1977).

[13]D. R. Taylor and E. Zaremba, Phys. Rev. B **23**, 3384 (1981).

[14]C. A. Hutchinson, Jr. and E. Wong, J. Chem. Phys. **29**, 754 (1958).

[15]J. W. Culvahouse and L. G. Pfortmiller, Bull. Am. Phys. Soc. **15**, 394 (1970).

[16]J. P. Boucher, H. Benner, F. Devreux, L. P. Regnault, J. Rossat-Mignod, C. Dupas, J. P. Renard, J. Bouillot, and W. G. Stirling, Phys. Rev. Lett. **48**, 431 (1982).

[17]S. E. Nagler, W. J. L. Buyers, R. L. Armstrong, and R. A. Ritchie, J. Phys. C **17**, 4817 (1984).