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Relaxation in the neighborhood of a magnetic impurity in the $s=\frac{1}{2}$ Heisenberg chain at high temperatures

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A Mori-Lee theoretic study of spin relaxation in the neighborhood of a magnetic impurity in the $s=\frac{1}{2}$ nearest-neighbor (NN) Heisenberg chain at high temperatures is presented. Our calculations suggest that in the limit of zero impurity coupling, the spectral function for the "surface spin" is consistent with a set of discrete frequencies given approximately by $w_n \approx [n(w_0+\frac{1}{4})-\frac{1}{4}]$ against a shallow continuum background, where $w_0 \approx 3J/4$ with $2J$ being the coupling between NN spins. The frequencies broaden as the impurity coupling is increased to the NN coupling.

The behavior of the dynamical spin-pair correlations (DSPC's) in the nearest-neighbor (NN) $s=1/2$ Heisenberg chain (HC) remains an open problem which has attracted considerable attention in recent years.[1] Often, however, some of the interesting realizations of HC's contain a small concentration of impurities,[2] which motivates us to study the DSPC in the *immediate neighborhood of an impurity*.

It has recently been suggested[3] that the DSPC for a *bulk* spin in the isotropic HC at $T\to\infty$ is consistent with an $e^{-\alpha t}$-like decay (at least for times $4<Jt<12$). It should, however, be mentioned that the magnitude of this DSPC at $Jt\to 12$ is $O(10^{-4})$ and hence a more precise calculation than in Ref. 3, which remains difficult to carry out, is called for to truly test this suggestion. Given this information, it is of interest to understand the relaxation processes near the imperfections (which break translation invariance) in the HC. Indeed, the single-impurity HC has attracted much attention in recent times.[4] The relaxation process near an impurity has been shown to differ drastically from that in the bulk for the $s=1/2$ XY chain.[5] It is expected [and has been demonstrated for $s=1/2$ XY chains at $T=\infty$ (Ref. 6)] that upon the absence of a "healing length" in the chain and at sufficient distances (of the order of $10-15$ spins) from the chain end for a semi-infinite chain, one should recover the bulk spin DSPC.

It is known that impurities and surface imperfections could lead to the presence of long-lived excitations in HC's.[2] We show that such long-lived excitations, which are characterized by well-defined peaks in the spectral functions (SF's) of the NN's of the impurity, become progressively dominant upon weakening the impurity coupling. One would expect that such dominant frequencies (coming from a few of the $N\to\infty$ spins) in a HC with few impurities will be difficult to extract from the inelastic neutron-scattering spectrum. We suggest that these frequencies could perhaps become observable upon carefully probing the shape of the SF as a function of frequency in dilute $s=1/2$ HC systems. A second way to determine the low-frequency peaks may be via Mössbauer effect spectroscopy, which allows one to probe into the local spin dynamics in a low-frequency window, on suitable systems.

Given how little is actually known about the DSPC's in HC's (Ref. 1) it is important to ask about how the DSPC's of the NN's of a single magnetic impurity differ from that of the bulk spins in the chain. This is precisely the problem we focus upon here. Our study therefore probes the spin dynamics in the immediate neighborhood of the impurity. The results are expected to be approximately valid in the low-impurity concentration regime ($<4\%$ say). The analysis is based on the continued fraction formalism (CFF) (Ref. 7) of Lee and others. Our study reveals the existence of characteristic frequencies associated with the parameter J', where $2J'$ describes the coupling between the impurity and its NN's while $2J$ describes the NN coupling between the other spins in the HC. The frequencies become progressively distinct as $J'\to 0$, i.e., the case of a chain that has been cut at site $j+1$. For simplicity the analysis is performed at $T=\infty$, at which the static correlations are trivial to evaluate. The calculations remain invariant up to $O(\beta)$, where $\beta=1/kT$. However, we expect, based on our recent studies of DSPC's for other simple low-dimensional spin systems,[8] that the features of the DSPC's in the neighborhood of the impurity are likely to possess similar behavior at finite T's in the HC. To our knowledge, this is one of the very few studies in which the high-T spin dynamics of a single-impurity system has been addressed.

We briefly summarize the CFF below. The details of our results on the DSPC's near the magnetic impurity are given thereafter. We close with a discussion of the implications of our calculation.

The calculation of the DSPC $\langle S_j^\alpha(t)S_j^\alpha\rangle/\langle(S_j^\alpha)^2\rangle$ where $\alpha=(x,y,z)$ for a HC with j being a NN of the impurity has been accomplished as follows. The CFF (Ref. 7) provides a prescription for constructing solutions to the Heisenberg equation of motion (HEM) for some dynamical variable and in turn for calculating the DSPC's involving the dynamical variable under study. Using the CFF we first express the spin operator $S_j^\alpha(t)$ as an orthogonal expansion in a Hilbert space [spanned by a complete set of orthogonal bases with the orthogonality being realized via a suitable scalar product, e.g., the Kubo scalar product (KSP) (Ref. 7)]. Thus,

$$S_j^\alpha(t)=\sum_{\nu=0}^{d-1} f_\nu a_\nu(t), \quad (1)$$

where f_ν's form a complete set of *time-independent* orthogonal bases and $a_\nu(t)$'s are their *time-dependent coefficients.* The orthogonality of the f_ν's are realized through the KSP which leads to a simple recurrence relation (RR), RR I, for the f_ν's given by

$$f_{\nu+1}=(i/\hbar)[H,f_\nu]+\Delta_\nu f_{\nu-1}, \quad (2)$$

where the square brackets denote commutators and $\Delta_\nu=(f_\nu,f_\nu)/(f_{\nu-1},f_{\nu-1})$, and for this problem which addresses high-T dynamics we choose $(X,Y)\equiv\langle XY^\dagger\rangle - \langle X\rangle\langle Y^\dagger\rangle$ (a special case of the KSP), and from now on we shall set $\hbar\equiv 1$. Since Eq. (2) above must satisfy the HEM, a second RR, RR II, emerges for the $a_\nu(t)$'s,

$$\Delta_{\nu+1}a_{\nu+1}=-da_\nu/dt+a_{\nu-1}, \quad \nu\geqslant 0, \quad a_{-1}\equiv 0. \quad (3)$$

Another way of writing RR II is by taking its Laplace transform and thereafter expressing $a_0(z)$ as a continued fraction (CF). Typically, $d\to\infty$ in Eq. (1) and $a_0(z)$, as a result, is an infinite CF (ICF) (Ref. 7) as described below:

$$a_0(z)=1/(z+\Delta_1/\{z+\Delta_2/[z+\Delta_3/(z+\cdots \text{to } \infty)]\}). \quad (4)$$

Realizing that $a_0(t)=4\langle S_j^\alpha(t)S_j^\alpha\rangle$ at $T=\infty$, it follows that the necessary information for computation of the Laplace transformed relaxation function given in Eq. (4) is contained in $\{\Delta_\nu\}$ which are, in general, functions of multipoint static correlations in the system. The calculation of the magnitudes of Δ_ν's is greatly simplified at high T's at which the traces over the spins that enter into the Δ_ν's become trivial to evaluate. The resultant dynamics describes a system with the eigenstates nearly equally Boltzmann weighted (unless $T=\infty$, when all the states are equally weighted).

The following summarizes the calculations to obtain the DSPC's for the NN's of a magnetic impurity at site $j+1$. The main focus of the study is to arrive at an estimation of Δ_ν's as a function of ν. As stated above, for most systems,[9] in the thermodynamic limit, $\nu\to\infty$. Even at $T=\infty$ the calculation of $\{\Delta_\nu\}$ is an impossibly difficult task for most many-body systems. Typically, the best one can do is to estimate the first few Δ_ν's and extrapolate therefrom, via some "reasonable ansatz," to guess the higher Δ_ν's. The dependence of the resulting DSPC on the details of the ansatz then becomes an important issue. The calculations presented here invoke such an ansatz, to be described below. We believe that the ansatz chosen is such that the DC's under study are essentially invariant upon minor amendments to the ansatz (such as varying the slope and the intercept by $<1-2$ %), at least for relatively short times (i.e., $Jt\sim 100$). The Δ_ν's thus obtained are then used to construct a finite CF (FCF) with a large number of levels and hence poles, this number being typically between 10^4 and 10^6 depending upon the convergence properties of the ICF (see Cai, Sen, and Mahanti in Ref. 7). Such large FCF's can be readily evaluated on a small supercomputer. The estimation of the CF and a subsequent numerical inverse Laplace transformation calculation (see Cai, Sen, and Mahanti in Ref. 7) of the calculated $a_0(z)$ yields the DSPC $4\langle S_j^\alpha(t)S_j^\alpha\rangle\equiv a_0(t)$ in the CFF, and the corresponding SF.

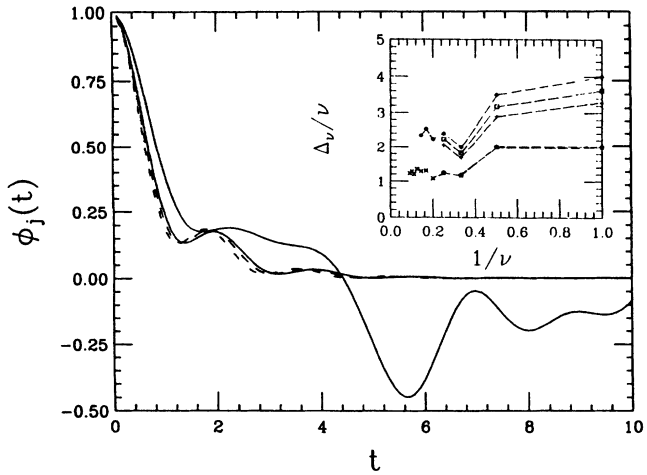

FIG. 1. Inset: Δ_ν/ν vs $1/\nu$ for $J'=0$, 0.1, 0.2, 0.9, 1.0 (from top to bottom). Main figure: The DSPC for $J'=0$ (fast relaxing solid line), 0.1 (dashed), 0.2 (dot-dashed), and 0.9 (slow relaxing solid line) cases. The results for $J'=1$ and $J'=0.9$ are practically indistinguishable.

As mentioned above, the challenge in the evaluation of the DSPC's for many-body systems concerns the calculation of the f_ν's and the Δ_ν's which enter via RR I above. The calculations quickly become algebraically challenging and it typically becomes tedious to compute the f_ν's and the Δ_ν's for $\nu\geqslant 4$ for spin systems with broken translation invariance. We have calculated the first four f_ν's and Δ_ν's *exactly* for the system under study which is characterized by

$$H=2J\sum_{i=1}^{N}\sum_{\alpha=1}^{3} S_i^\alpha S_{i+1}^\alpha-2J'\sum_{\alpha=1}^{3} S_{j+1}^\alpha S_{j+2}^\alpha, \quad (5)$$

with the impurity site being at $j+1$ and the impurity coupling being $2(J-J')$. The calculations have been carried out by choosing $f_0=S_j^x(0)\equiv S_j^x$ in Eq. (1) and then generating the higher f_ν's via RR I. The detailed expressions for the f_ν's are long and will be reported in a detailed paper on impure $S=1/2$ chains.[10] Our choice of f_0 renders the $a_0(t)=\langle S_j^x(t)S_j^x\rangle/\langle(S_j^x)^2\rangle\equiv\phi_j(t)$, which is the quantity of interest. The Δ_ν's thus obtained at $T=\infty$ are described in Fig. 1 (see inset) for various values of J' with $J\equiv 1$. The result for the $J'=0$ case (which renders S_j^x a bulk spin) was published recently.[3] The $J'=1$ case is less well explored. Although the Δ_ν's given here for $J'=1$ have been reported by Stolze *et al.*,[1] a detailed calculation of the corresponding surface spin relaxation function in a semi-infinite HC has been unavailable. The DSPC's of the NN's of an impurity spin described by cases with $0<J'<1$ are not known at all. We address the spin dynamics in this regime by carrying out a perturbative treatment of the ICF against the $J'=0$ and the $J'=1$ cases. The main results of our calculation are summarized below.

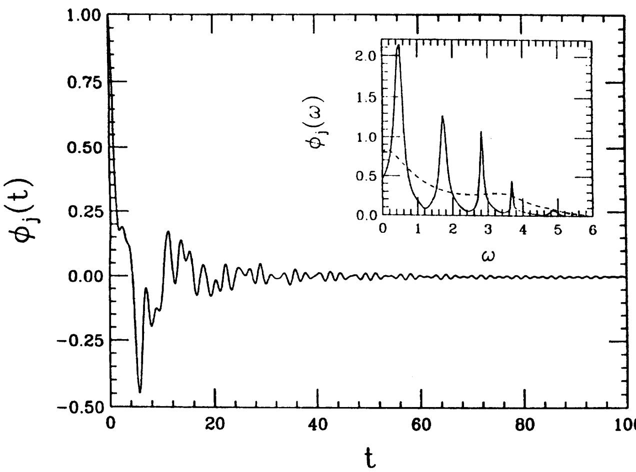

FIG. 2. Main figure: DSPC vs time for the $J'=0.9$ case shown up to $t=100$. Note the long-lived oscillations suggestive of an oscillatory algebraic decay. Inset: SF corresponding to $J'=0.9$ (solid), 0 (dotted), 0.1 (dashed).

First of all, recall that the time-dependent behavior of $\phi_j(t)$ for $J'=0$ exhibits $e^{-\alpha t}$-like decay at "intermediate times" ($4<Jt<12$).[3] The oscillatory behavior of $\phi_j(t)$ for the $J'=0$ case becomes more pronounced when $J'>0$, i.e., when an impurity is present. We present our calculations for $\phi_j(t)$ with $J'=0$, 0.1, and 0.2 in Fig. 1. We also present our results for the weak-coupling limit of the impurity with $J'=0.9$ in Fig. 2. These calculations have been carried out perturbatively by evaluating Δ_1 through Δ_4 exactly for the chosen values of J' and then by replacing Δ_5 through Δ_∞ using the $J'=0$ case results for the small J' cases and by the $J'=1$ case results for the "large" J' case. The extrapolation schemes used for small J' in our calculations are: (i) $J'=0.1$ case, $\Delta_\nu=2.50(\nu-4)+8.93$, (ii) $J'=0.2$ case, $\Delta_\nu=2.30(\nu-4)+8.23$, (iii) $J'=0.3$ case, $\Delta_\nu=2.18(\nu-4)+7.49$ for $\nu\geqslant 4$. The extrapolation scheme invoked in Ref. 3 for the $J'=0$ case was $\Delta_\nu=2.65(\nu-7)+17.00$ for $\nu\geqslant 8$. The scheme used for the $J'=0.9$ case study used the exactly known Δ_ν's for the $J'=1$ case for $5\leqslant\nu\leqslant 11$ and the extrapolation scheme $\Delta_\nu=1.20(\nu-11)+1.0$ for $\nu\geqslant 12$ while that used for computation of the case $J'=1$ consisted of the exact Δ_ν's for $1\leqslant\nu\leqslant 11$ and $\Delta_\nu=1.20(\nu-11)+1.0$ for $\nu\geqslant 12$. The CF's obtained using these Δ_ν's were truncated at the 10000th and 10001st levels in two separate calculations for each case. We found no evidence of any *odd-even effect* in $\phi_j(t)$ for the cases studied, which in turn suggested that the estimated behaviors of the CF's studied were stable against truncation effects within the accuracy of our calculations (typically about 10^{-4}). The results are expected to be reliable for $Jt\leqslant 100$ and when asymptotic dynamics is not considered, which in our view can *only* be studied in the presence of an *exact solution.*

This form of perturbation theory is known to be reliable[11] when the corrections to the Δ_ν's with respect to the "ideal" Δ_ν's grow linearly (or sublinearly) with ν, a condition which appears to hold here for the lower Δ_ν's. As is well known, corrections to the first few levels of the ICF can play a more significant role in determining the z-dependent behavior of the ICF than the levels deeper down.[11]

The behavior of $\phi_j(t)$ for small J''s reveals the presence of some oscillations which become progressively stronger as J' is increased. The behavior of $\phi_j(t)$ becomes distinctly oscillatory with remarkably slow decay of $\phi_j(t)$ in time as $J'\rightarrow 1$. Our calculations reveal very little difference between the $\phi_j(t)$ obtained for the $J'=1$ and $J'=0.9$ cases. The large J' case suggests the onset of an oscillatory-algebraic decay of $\phi_j(t)$. Given the times up to which Jt has been studied here it remains difficult to reliably draw any conclusions regarding the nature of the decay of $\phi_j(t)$ in t. It appears, however, that the decay is oscillatory-algebraic in nature for large t. Our calculations also provide strong evidence for a crossover regime from an overall exponential-like decay of $\phi_j(t)$ at $J'\rightarrow 0$ to an overall oscillatory-algebraic decay of $\phi_j(t)$ at $J'\rightarrow 1$. This observation suggests that $J'=0.5$ is probably an interesting regime to study. A reliable calculation with $J'=0.5$, however, remains to be carried out at present due to a lack of knowledge of higher Δ_ν's which appears to be essential for such a study.

The SF corresponding to $\phi_j(t)$, i.e., $\phi_j(\omega)$ is given in Fig. 2 (inset). An interesting feature to observe in Fig. 2 (inset) is that the presence of the impurity leads to the presence of broad maxima in $\phi_j(\omega)$ at small ω ($\omega\approx 0.2$) and at large ω ($\omega\approx 3.4$). The high-frequency mode is obviously related to the period of the small oscillations that develop at short times in $\phi_j(t)$ with a characteristic period of $2Jt<2$, or $Jt<1$. The slight reduction in the periodicity of the oscillations in $\phi_j(\omega)$ presumably stems from $J'<1$. The long time behavior of $\phi_j(t)$ still appears to be reasonably consistent with $e^{-\alpha t}$-like decay, although the oscillations make it difficult to make any claim in this regard. In fact, a similar problem also appears when interpreting the long time behavior of $\phi_j(t)$ for the bulk spin case and we had reported that the results were roughly consistent with $t^{-\gamma}$-type decay with $\gamma\approx 0.77$. The dynamical problem for the NN of the impurity spin becomes very rich as $J'\rightarrow 1$. We study this case via perturbation about the $J'=1$ case. It turns out that for $J'=0.9$, it is hard to distinguish between the $J'=0.9$ and 1 cases within the limits of our resolution. The frequency spectrum $\phi_j(\omega)$ for the $J'\rightarrow 1$ case exhibits a set of well-defined peaks. Except for the first peak, it appears that the peak positions are well approximated by the relation $\omega_n\approx n(\omega_0+1/4)-1/4$ for our system, where $\omega_0\approx 3J/4$. The first peak which reveals the lowest dominant frequency may be the most difficult one to determine unequivocally in the absence of an analytic solution to the relaxation function. We find that this peak is located at $\omega=0.45$, which is lower than $\omega_0=0.75$ predicted by our suggested formula. The higher frequencies are, however, much better approximated by the above-mentioned relation.

To conclude, we have shown via approximate analytical calculations that the presence of a magnetic impurity in the HC profoundly affects the relaxation of its NN's. Our calculations invoke a simple ansatz, that Δ_ν's grow linearly with-respect to ν for large ν, which happens to hold true for many $S=1/2$ systems at high and low T's (see Sen *et al.* in J. Appl. Phys.[8]), although other patterns exist. In particular, our results demonstrate that the frequency spectrum of the DSPC of the NN's of a weakly coupled nonmagnetic impurity in a HC is characterized by a sharp set of peaks of progressively diminishing strengths with increasing frequency.

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