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Energy Transport at Finite Temperatures in Isotropic Magnetic Chains with $S = \frac{1}{2}$

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Energy transport is shown to be nondiffusive at finite temperatures in a magnetic chain of spin-$\frac{1}{2}$ particles with isotropic nearest-neighbor Heisenberg interactions in zero external field. In a uniform magnetic field, the Zeeman energy ensures that energy diffusion is reestablished at all temperatures if spin diffusion is present. At infinite temperatures the introduction of weak next-nearest-neighbor interactions also reestablishes energy diffusion. We use the Mori-Kawasaki expression for the diffusion constant in terms of the second and fourth moments of the time Fourier transform of the relaxation function. Investigation of the sixth moment indicates that the time derivative of the energy density exhibits diffusive behavior even though the energy density does not.

It has been shown[1] that, at infinite temperatures, energy transport is nondiffusive in an isotropic magnetic chain of spins with $S = \frac{1}{2}$ and zero external field. In this paper we show it is true at all temperatures if one uses an approximate expression for the inverse decay time based on the second and fourth moments of the energy relaxation function.

The Hamiltonian for our system is

$$H = -2J \sum_{n=0}^{N-1} \vec{S}_n \cdot \vec{S}_{n+1} + \mathcal{H} \sum_{n=0}^{N-1} S_n^z$$
$$= H_x + H_z \ , \tag{1}$$

where H_x is the exchange energy and H_z is the Zeeman energy. The relevant relaxation function for energy transport at finite temperature is

$$R(k,t) = \{h(k,t),\, h(-k,0)\}\ \{h(k,0),\, h(-k,0)\}^{-1}, \tag{2}$$

where $h(k,t)$ is the Fourier transform of the energy density

$$h(k,t) = \textstyle\sum_n e^{ikan} h_n(t) \ ,$$
$$h_n(t) = -J[\vec{S}_n(t) \cdot \vec{S}_{n+1}(t) + \vec{S}_n(t) \cdot \vec{S}_{n-1}(t)] + \mathcal{H} S_n^z(t) \ , \tag{3}$$
$$\{A, B\} = \int_0^\beta d\lambda\, \langle e^{\lambda H} A\, e^{-\lambda H} B\rangle - \beta \langle A\rangle \langle B\rangle \ ,$$

and

$$\langle O\rangle = \text{Tr}\, e^{-\beta H} O / \text{Tr}\, e^{-\beta H} .$$

The lattice constant is a and $\beta = (k_B T)^{-1}$ where k_B is Boltzmann's constant and T is the temperature. If diffusion is present, then for small k the time dependence of $R(k,t)$ is approximately[2]

$$R(k,t) = \exp[-|t|\, \Gamma(k)]. \tag{4}$$

As discussed in Ref. 3, an approximate expression for $\Gamma(k)$ is

$$\Gamma(k) = [\pi/2]^{1/2} M_2(k) [M_2(k)/M_4(k)]^{1/2}, \tag{5}$$

where

$$M_{2n}(k) = \left[\left(\frac{1}{i} \frac{\partial}{\partial t} \right)^{2n} R(k,t) \right]_{t=0} . \tag{6}$$

Energy diffusion is said to occur when the average of the energy density $\bar{h}(r,t)$, obeys a diffusion equation for long-wavelength disturbances

$$\frac{\partial}{\partial t} \bar{h}(r,t) = D \nabla^2 \bar{h}(r,t) .$$

This implies that $\Gamma(k)$ is Dk^2 for small k. D is the diffusion constant. For zero external field, we shall show $M_2(k) = k^2 a(k)$ and $M_4(k) = k^4 b(k)$ for small k. In addition, $a(O)$ is shown to be finite at infinite temperatures, and $b(O)$ is proved to be finite for all temperatures. Thus one expects Γ to be proportional to k for small k in contrast to the k^2 dependence for diffusion.

Convenient expressions for the required moments are

$$M_2(k) = C(k)^{-1} \textstyle\sum_n e^{ikan} \{[H,\, [H, h_n]],\, h_0\} \ , \tag{7}$$

$$M_4(k) = C(k)^{-1} \textstyle\sum_n e^{ikan} \{[H,\, [H, h_n]], [H, [H, h_0]]\} \ , \tag{8}$$

and

$$C(k)=\sum_n e^{ikan}\{h_n, h_0\} . \tag{9}$$

We use periodic boundary conditions so that $S_{N+n}=S_n$.

First consider the case with zero external field ($\mathcal{H}=0$). The commutators have been calculated by Redfield and Yu.[4] For the spin-$\frac{1}{2}$ chain with nearest-neighbor interactions they take the form

$$[H_x,[H_x,h_n^x]]=P_n , \tag{10}$$

where

$$P_n=2J^3\{T_n-T_{n-1}-T_{n-2}+T_{n-3}\} , \tag{11}$$

with

$$T_n=\vec{S}_{n+1}\cdot\vec{S}_{n+2}+2\vec{S}_n\times\vec{S}_{n+1}\cdot\vec{S}_{n+2}\times\vec{S}_{n+3} . \tag{12}$$

From Eq. (11) we see that $P(k)$ vanishes at least as fast as k^2 for k small. Substituting these into M_2 and M_4 we have ($\mathcal{H}=0$)

$$M_2(k)=2^5C(k)^{-1}J^4\sin^2(ka/2)\cos^2(ka/2) \times\sum_n e^{ikan}\{T_n, \vec{S}_1\cdot\vec{S}_2\}' , \tag{13}$$

$$M_4(k)=2^8C(k)^{-1}J^6\sin^4(ka/2)\cos^2(ka/2) \times\sum_n e^{ikan}\{T_n, T_0\}' , \tag{14}$$

$$C(k)=2^2J^2\cos^2(ka/2)\sum_n e^{ikan}\{\vec{S}_n\cdot\vec{S}_{n+1}, \vec{S}_0\cdot\vec{S}_1\} , \tag{15}$$

where

$$\{A,B\}'=\{A,B\}+\beta\langle A\rangle\langle B\rangle .$$

In the infinite temperature limit

$$C(k)\rightarrow\tfrac{3}{4}J^2\beta\cos^2(ka/2) ,$$

$$M_2(k)\rightarrow 8J^2\sin^2(ka/2) , \tag{16}$$

$$M_4(k)\rightarrow 128J^4\sin^4(ka/2) , \tag{17}$$

in agreement with Ref. 1.

In $M_4(k)$ appears a quantity of the form

$$\sum_n e^{ikan}\{A_n, A_0\}'=N^{-1}\{A(k),A(k)^+\}' . \tag{18}$$

Using the method of Mermin and Wagner[5] it is straightforward to show that for finite temperatures $\{A,A^+\}'\geq 0$ with the equality if and only if $A\equiv 0$.[6] In our case $A(k)\neq 0$. Furthermore $C(O)$ is the specific heat which will be greater than zero. Thus, $M_4(k)$ vanishes as k^4 for all temperatures. Diffusion requires that $\Gamma(k)$ vanish as k^2 which together with $M_4(k)\sim k^4$ and Eq. (5) requires that $M_2(k)$ vanish as $k^{8/3}$. This nonanalytic behavior as a function of k seems quite unlikely at any temperature for systems with short-range interactions. We conclude that energy transport by diffusion in zero external field is impossible at all temperatures if we use moments [Eq. (5)] to calculate the damping constant $\Gamma(k)$.

Next let us apply a uniform magnetic field ($\mathcal{H}\neq 0$). The commutators in (7) and (8) become

$$[H,[H,h_n]]=P_n+\mathcal{H}Q_n , \tag{19}$$

where

$$Q_n=[H_x,[H_x,S_n^z]].$$

Again using expressions derived by Redfield and Yu[4] we have

$$Q_n=2V_n-V_{n+1}-V_{n-1}+U_n-U_{n-1} , \tag{20}$$

where

$$V_n=2J^2S_n^z(1+2\vec{S}_{n+1}\cdot\vec{S}_{n-1}) \tag{21}$$

and

$$U_n=4J^2(S_{n+2}^z-S_{n-1}^z)\vec{S}_n\cdot\vec{S}_{n+1} . \tag{22}$$

From (20) we see that $Q(k)$ vanishes at least as fast as k.

In $M_4(k)$ we will have

$$\{P_n+\mathcal{H}Q_n,\ P_0+\mathcal{H}Q_0\}'=\{P_n,P_0\}'+\mathcal{H}\{Q_n,P_0\}' +\mathcal{H}\{P_n,Q_0\}'+\mathcal{H}^2\{Q_n,Q_0\}' . \tag{23}$$

Thus, the Fourier transform of the terms of (23) will go to zero at least as fast as k^4, k^3, k^3, and k^2, respectively. The contribution of the final term of (23) may be written for small k as

$$\mathcal{H}^2\sum_n e^{ikan}\{Q_n,Q_0\}'\rightarrow\mathcal{H}^2k^2a^2\{U(k=0),U(k=0)^+\}' . \tag{24}$$

Since $U(k=0)\neq 0$, we see $M_4(k)$ vanishes as k^2 for all temperatures.

In $M_2(k)$ we will have

$$\{P_n+\mathcal{H}Q_n, h_0^x+\mathcal{H}S_0^z\}'=\{P_n,h_0^x\}'+\mathcal{H}\{P_n,S_0^z\}' +\mathcal{H}\{Q_n,h_0^x\}'+\mathcal{H}^2\{Q_n,S_0^z\}' . \tag{25}$$

From (11) the Fourier transform of the first two terms in (25) vanish at least as fast as k^2. From (20)–(22) we can also show that

$$\sum_n e^{ikan}\{Q_n,h_0^x\}'=4\sin^2(ka/2)N^{-1}\{V(k),\ h^x(-k)\}' -16J^3\sin ka\sum_n\sin(kan)\{S_{n+2}^z\vec{S}_n\cdot\vec{S}_{n+1}, \vec{S}_0\cdot\vec{S}_1\}' \tag{26}$$

and

$$\sum_n e^{ikan}\{Q_n,S_0^z\}'=4\sin^2(ka/2)N^{-1}\{V(k),S^z(-k)\}' +(1-e^{ika})8iJ^2\sum_n\sin(kan)\{S_{n+2}^z\vec{S}_n\cdot\vec{S}_{n+1}, S_0^z\}' . \tag{27}$$

Thus, $M_2(k)=f_2(k)k^2$ and $M_4(k)=f_4(k)k^2$, where $f_4(O)$ is finite for all temperatures. At infinite temperature

$$C(O)=\tfrac{1}{4}\beta\{3J^2+\mathcal{H}^2\} , \tag{28a}$$

$$f_2(O)=2a^2J^2, \tag{28b}$$

$$f_4(O)=4a^2J^4\mathcal{H}^2(3J^2+\mathcal{H}^2)^{-1} , \tag{28c}$$

so $\Gamma(k)=D_E k^2$ which indicates a diffusive mode of energy transport as noted by Huber[7] with

$$D_E=\sqrt{\pi}\, a^2 J\{3J^2+\mathcal{H}^2\}^{1/2}\mathcal{H}^{-1} .$$

We have no reason to expect $f_2(O)$ to vanish at finite temperatures, and so we expect energy diffusion to occur at all temperatures in a uniform external field.

To compare D_E at infinite temperatures with the spin diffusion constant D_S we note that D_S is given by Γ_S/k^2 where Γ_S is given by Eq. (5) if one replaces h_n by S_n^z in Eqs. (7)–(9). At infinite temperatures one finds

$$C^S(k)\rightarrow \beta/4\ , \tag{29a}$$

$$M_2^S(k)\rightarrow 2k^2a^2J^2\ , \tag{29b}$$

$$M_4^S(k)\rightarrow 4k^2a^2J^4\ . \tag{29c}$$

Thus, we have $D_S=\sqrt{\pi}\, a^2 J$ and

$$D_E=D_S\{3J^2+\mathcal{H}^2\}^{1/2}\mathcal{H}^{-1}\geq D_S\ .$$

We see that D_E approaches D_S for large magnetic fields, as we expect, and for small fields $D_E\gg D_S$.

Next, we consider the effects of introducing next-nearest-neighbor interactions. The Hamiltonian is

$$H=-\sum_{l,n} J_{ln}\vec{S}_n\cdot\vec{S}_l\ .$$

For arbitrary $J_{ln}=J_{nl}$ satisfying $J_{ll}=0$ and arbitrary S, we find

$$\begin{aligned}[H,[H,h_n]]=2\sum_{m,l,r}(n,m,r,l)\{&J_{mn}J_{lr}J_{nr}(1-\delta_{nl})\\ &+J_{nl}J_{lr}J_{ml}(1-\delta_{mn})-J_{mn}J_{nr}J_{ln}(1-\delta_{lr})\\ &-J_{rl}J_{mn}J_{lm}(1-\delta_{nl})\}\ ,\end{aligned} \tag{30}$$

where

$$(n,m,r,l)=\vec{S}_n\times\vec{S}_m\cdot\vec{S}_r\times\vec{S}_l+\vec{S}_r\times\vec{S}_l\cdot\vec{S}_n\times\vec{S}_m$$

and where

$$h_n=-\textstyle\sum_l J_{ln}\vec{S}_l\cdot\vec{S}_n\ .$$

This generalizes the result of Redfield and Yu[4] to general S and to lattices which have three spins which are mutually near neighbors. For a chain we have

$$J_{ln}=J(\delta_{l,n+1}+\delta_{l,n-1})+J'(\delta_{l,n+2}+\delta_{l,n-2}).$$

From (8) we see that for small k

$$M_4(k)=C(O)^{-1}k^2N^{-1}\{\textstyle\sum_n nA_n,\sum_m mA_m\}'+O(k^3)\ ,$$

where $A_n=[H,H,h_n]]$. For a spin-$\frac{1}{2}$ chain at infinite temperatures, we find to lowest order in J' and k

$$M_4(k)\rightarrow 24(JJ')^2k^2a^2\ ,$$

which implies

$$\Gamma(k)\rightarrow\left(\frac{\pi}{6}\right)^{1/2}\frac{J^2}{J'}\ k^2a^2\ .$$

Thus, the next-nearest-neighbor interactions reestablishes energy diffusion if nearest-neighbor interactions are present. On the other hand, if $J=0$ and $J'\neq 0$, then energy diffusion is not possible. This follows because a chain with interactions between mth nearest neighbors is isomorphic to a chain (or a collection of chains which do not interact with each other) with nearest-neighbor interactions which was discussed earlier.

Let us now return to the question of self-consistency in the use of Eq. (5) for the diffusion constant.

Mori and Kawasaki's derivation assumes that if diffusion exists, then, because of kinematic slowing down, $R(k,t)$ decays more slowly than the relaxation function for $\dot{h}(k,t)$,

$$F(k,t)=\{\dot{h}(k,t),\dot{h}(-k,0)\}\{\dot{h}(k,0),\dot{h}(-k,0)\}^{-1}\ . \tag{31}$$

They also assume that the time Fourier transform of this, $F(k,\omega)$, is a Gaussian,

$$F_G(k,\omega)=\{2\pi\langle\omega^2\rangle\}^{-1/2}\exp\{-0.5\omega^2\langle\omega^2\rangle^{-1}\}\ , \tag{32}$$

where

$$\langle\omega^n\rangle=\int_{-\infty}^{\infty}d\omega\,\omega^nF(k,\omega)=M_{n+2}/M_2\ .$$

When diffusion is present $M_2\sim k^2$ and $M_4\sim k^2$, so the ratio of a characteristic time of $F(k,t)$, $\langle\omega^2\rangle^{-1/2}$, to a characteristic time of $R(k,t)$, Γ^{-1}, is

$$t_F/t_R\sim M_2^2/M_4\sim k^4/k^2\sim k^2\ .$$

Thus, $t_F\ll t_R$ for small k and the assumptions are self-consistent. On the other hand, for the spin-$\frac{1}{2}$ chain with no external field we have

$$t_F/t_R\sim k^4/k^4\sim 1$$

and the characteristic times are comparable, and thus $R(k,t)$ does not decay more slowly then $F(k,t)$ and we have an inconsistency. This is another way of saying that energy diffusion does not exist.

One may generalize the form taken for $F(k,\omega)$ by expanding it in a Gram-Charlier series[8]

$$F(k,\omega)=F_G(k,\omega)\{1+C_4H_4(x)+\cdots\}\ , \tag{33}$$

where

$$H_4(x)=x^4-6x^2+3\ ,$$

with

$$x=\omega\langle\omega^2\rangle^{-1/2}$$

and

$$C_4=\frac{1}{8}\left\{\frac{\langle\omega^4\rangle}{3\langle\omega^2\rangle^2}-1\right\}\ . \tag{34}$$

Now $\langle\omega^4\rangle$ requires a knowledge of M_6. We find, for small k and all temperatures,

$$M_6(k)\rightarrow\frac{2^4J^6k^4a^4}{NC(O)}\ \{Y(k),Y(k)^+\}'\ , \tag{35}$$

where

$$Y_n = J\vec{S}_n \times \vec{S}_{n+3} \cdot (\vec{S}_{n+1} - \vec{S}_{n+2}) \ .$$

Thus, $M_6(k) \sim k^4$ for all temperatures. In the infinite temperature limit $M_6 \rightarrow 4J^6k^4a^4$. Thus, we conclude that C_4 diverges as k approaches zero. This is another indication that energy diffusion does not exist. So far we have used the Mori-Kawasaki expression for the diffusion constant. de Gennes[9] arrived at a similar expression for Γ by assuming a cutoff Lorentzian form for the Fourier transform of $R(k, t)$:

$$R(k, \omega) = \frac{d}{\pi} \frac{\Gamma(k)}{\omega^2 + \Gamma(k)^2} \quad \text{for } |\omega| \leq s, \tag{36a}$$

$$R(k, \omega) = 0 \quad \text{for } |\omega| > s \ . \tag{36b}$$

From the condition $R(k, t=0) = 1$ and expressions for M_2 and M_4, one may evaluate Γ and s. If diffusion occurs, $M_2 \sim k^2 \sim M_4$ and one finds

$$\Gamma_{DG} = \frac{\pi}{2\sqrt{3}} \left\{\frac{M_2^3}{M_4}\right\}^{1/2} ,$$

$$s = \{3M_4/M_2\}^{1/2} ,$$

where $\Gamma \ll s$. However, if $M_4 \leq 5.6M_2^2$, one can show that the cutoff Lorentzian will not fit M_2 and M_4 for real positive values of d, Γ, and s. At infinite temperatures in a spin-$\frac{1}{2}$ chain with nearest-neighbor interaction, $M_4 = 2M_2^2$ so the cutoff Lorentzian for $R(k, \omega)$ is not possible.

A similar criterion for energy diffusion has been proposed by Bennett.[10] The moment fluctuation ratio

$$\mathcal{R}(k) = M_2^2 \{M_4 - M_2^2\}^{-1}$$

becomes very small if diffusion is present and becomes very large if a propagating mode is present. For the spin-$\frac{1}{2}$ chain where $M_2 \sim k^2$ and $M_4 \sim k^4$, the ratio $\mathcal{R}(k)$ is independent of k for small k for all temperatures. At infinite temperature $\mathcal{R}(k) = 1$, which again indicates that energy diffusion is not present. Unless $\mathcal{R}(k)$ is strongly temperature dependent, one expects energy diffusion to be absent at all temperatures by this criterion also.

Finally it is worth noting that for the isotropic spin-$\frac{1}{2}$ chain we have $M_2 \sim k^2$, $M_4 \sim k^4$, and $M_6 \sim k^4$ for all temperatures. Thus, the relaxation function for $\dot{h}(k, t)$, that is, $F(k, t)$, exhibits diffusive behavior and thus one may assume that the time Fourier transform of $\{\ddot{h}(k, t), \ddot{h}(-k, 0)\}$ is a Gaussian.

Proceeding as before we find that if $F(k, t) = e^{-|t|\tilde{\Gamma}(k)}$, then

$$\tilde{\Gamma}(k) = \left(\frac{\pi}{2}\right)^{1/2} \langle\omega^2\rangle \left\{\frac{\langle\omega^2\rangle}{\langle\omega^4\rangle}\right\}^{1/2}$$

$$= \left(\frac{\pi}{2}\right)^{1/2} \frac{M_4}{M_2} \left\{\frac{M_4}{M_6}\right\}^{1/2} \ . \tag{37}$$

At infinite temperatures we find $\tilde{\Gamma} = 4Jk^2a^2\sqrt{\pi}$.

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