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Impurity Dynamics in a One-Dimensional Chain[1]

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The behavior of an impurity spin in a one-dimensional chain is investigated using the Glauber model. Two different types of impurities are considered and exact expressions for the average spin of the impurity, given that the impurity was initially excited out of equilibrium, are found. The behavior of these models is discussed in detail and their relevance to other physical situations is considered.

KEY WORDS: Impurity spin dynamics; Glauber kinetic Ising model.

1. INTRODUCTION

Professor Glauber once apologized to students for having the "Ising disease," that is, a fascination with this very simple model system.(1) This disease is caused chiefly by the prospect of exact mathematical solution of the models. Professor Glauber's kinetic Ising model is a prime example since analytic expressions can be found for many quantities of interest.(2)

In this paper we consider the dynamics of an impurity spin in a one-dimensional chain of spins. The dynamics of this system is modeled by the Glauber master equation for single, uncorrelated spin–flips. The resulting equations for the average spin can be reduced to a simple form and solved exactly.

The main question we address with this model is: what effect does the critical slowing down of a system near a phase transition have on an impurity coupled to it? Previous studies of dynamic Ising models with quenched impurities have focused on the behavior of the system averaged

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over the locations of a finite concentration of impurities.(3,4) Although the one-dimensional Ising model does not have a nonzero critical temperature, the correlation length of the pure system

$$\xi = 1/\left[1 - \tanh(\beta J)\right] \cong \tfrac{1}{2} e^{2\beta J} \tag{1.1}$$

can be made as large as desired by increasing the spin coupling constant J. The relaxation time for this system also increases as

$$\tau = 1/\left[1 - \tanh(2\beta J)\right] \tag{1.2}$$

so the system can be made as sluggish as desired as J increases.

In addition to being a model for the dynamics of a spin system, the Glauber model has been employed in other contexts, for example in the dynamics of the helix-coil transition in a DNA molecule(5) and the effect of interactions between enzymes in a chain.(6) Our original motivation for studying this system was as a model for a chemical reaction occurring in a solvent near a critical point. Ising models have long been used in the study of liquid–gas and binary mixture phase transitions. However, only under very restricted circumstances will the Glauber model be an acceptable model of the *dynamics*, for example, of binary fluid phase separation. Normally, the fractions of the component species are conserved quantities. The Glauber, single spin–flip model does not conserve spin. The Glauber model will only be relevant in cases where the two component species can freely interconvert. Our model, therefore, may be used when a unimolecular chemical reaction is occurring in a solvent that can itself interconvert between two chemically distinct species, and these two species are undergoing a phase separation. This rather unconventional phase transition has been discussed, thermodynamically, by Gitteman and Steinberg.(7) We will return to this application in the discussion, and focus on the results obtained from the mathematical model.

The outline of this paper is as follows. In Section 2 we sketch the derivation of the Glauber model, with special attention paid to the modifications required to treat the impurity. In Section 3, exact solutions are given for two different types of impurities. Section 4 contains a discussion of these expressions for intermediate and asymptotic times, and we close with a brief discussion in Section 5.

2. FORMULATION OF THE MODEL

The derivation, or motivation, of Glauber's master equation and the equation obeyed by the various moments has been discussed by many authors.(2,3,8) Here we will briefly recapitulate only those aspects that are modified by the introduction of an impurity. We consider a chain of spins,

σ_i, each allowed only the values $\sigma = \pm 1$. We then adopt a master equation for the rate of change of the probability $P(\sigma_1, \sigma_2, \ldots, \sigma_N; t)$ for a given configuration of spins $\{\sigma_1, \sigma_2, \ldots, \sigma_N\}$ at time t. We denote by $w_i(\sigma_i)$ the probability that the ith spin flips from σ_i to $-\sigma_i$ while the remaining spins stay fixed. This probability will in general be function of all the spins. The master equation is

$$\frac{d}{dt} P(\sigma_1, \sigma_2, \ldots, \sigma_N; t) = -\left[\sum_j w_j(\sigma_j)\right] P(\sigma_1, \ldots, \sigma_N; t) + \left[\sum_j w_j(-\sigma_j) P(\sigma_1, \ldots, -\sigma_j, \ldots, \sigma_N; t)\right] \tag{2.1}$$

The choice of $w_i(\sigma_i)$ is still arbitrary. The Glauber model consists of choosing the form

$$w_j(\sigma_j) = \tfrac{1}{2}\alpha_j\left[1 - \tfrac{1}{2}\sigma_j(\gamma_{jj-1}\sigma_{j-1} + \gamma_{jj+1}\sigma_{j+1})\right] \tag{2.2}$$

where we have generalized the expression to allow for different couplings (γ's) between the sites. In this expression α_i is the spin-flip rate for the ith spin and in the absence of any coupling with its neighbors, α_i is the decay rate of the average of the ith spin.

Following Glauber, we now choose the γ's so that the equilibrium distribution obeys Boltzmann statistics,

$$\frac{P_{\text{eq}}(\sigma_1, \ldots, -\sigma_j, \ldots, \sigma_N)}{P_{\text{eq}}(\sigma_1, \ldots, \sigma_j, \ldots, \sigma_N)} = \frac{e^{-\beta H[\sigma_1, \ldots, -\sigma_j, \ldots, \sigma_N]}}{e^{-\beta H[\sigma_1, \ldots, \sigma_j, \ldots, \sigma_N]}} \tag{2.3}$$

where

$$H(\sigma_1, \ldots, \sigma_N) = -\sum_{i=1}^{N-1} J_{i,i+1}\sigma_i\sigma_{i+1} \tag{2.4}$$

From this requirement it follows that

$$\begin{aligned}\frac{w_j(\sigma_j)}{w_j(-\sigma_j)} &= \frac{e^{-\beta H(\sigma_1, \ldots, -\sigma_j, \ldots, \sigma_N)}}{e^{-\beta H(\sigma_1, \ldots, \sigma_j, \ldots, \sigma_N)}} = \frac{e^{-\beta J_{jj-1}\sigma_{j-1}\sigma_j - \beta J_{jj+1}\sigma_{j+1}\sigma_j}}{e^{\beta J_{jj-1}\sigma_{j-1}\sigma_j + \beta J_{jj+1}\sigma_{j+1}\sigma_j}} \\ &= \frac{1 - \sigma_j \tanh(\beta J_{jj-1}\sigma_{j-1} + \beta J_{jj+1}\sigma_{j+1})}{1 + \sigma_j \tanh(\beta J_{jj-1}\sigma_{j-1} + \beta J_{jj+1}\sigma_{j+1})}\end{aligned} \tag{2.5}$$

which implies that if $w_j(\sigma_j)$ has the form of Eq. (2.2) then

$$\gamma_{jj-1} = \tanh(\beta J_{jj-1} + \beta J_{jj+1}) - \tanh(\beta J_{jj-1} + \beta J_{jj+1}) \tag{2.6}$$

$$\gamma_{jj+1} = \tanh(\beta J_{jj-1} + \beta J_{jj+1}) + \tanh(\beta J_{jj-1} - \beta J_{jj+1}) \tag{2.7}$$

We will focus our attention on a single impurity, which we locate at the origin. We will consider the limit of a very large or infinite system. We designate the unperturbed coupling constant as J and the impurity coupling constant as J'. This results in the following set of γ's:

$$\gamma_{01} = \gamma_{0-1} = \tanh(2\beta J') \tag{2.8}$$

$$\gamma_{10} = \gamma_{-10} = \tanh[\beta(J+J')] + \tanh[\beta(J-J')] \tag{2.9}$$

$$\gamma_{12} = \gamma_{-1-2} = \tanh[\beta(J+J')] - \tanh[\beta(J-J')] \tag{2.10}$$

and for all others

$$\gamma_{i,i-1} = \gamma_{i,i+1} = \tanh(2\beta J) \tag{2.11}$$

The structure of the transition rates is such that even though only two constants in the Hamiltonian are changed, five coupling constants in the master equation are changed.

One pleasant feature of this choice of transition rates is that the equations for the average spin $s_i = \langle \sigma_i \rangle$ are decoupled from the higher moments. The equations of motion for the average spin become

$$\frac{ds_i}{dt} = -\alpha_i s_i + \alpha_i \frac{1}{2} \left[\gamma_{i,i-1} s_{i-1} + \gamma_{ii+1} s_{i+1} \right] \tag{2.12}$$

Equation (2.12) together with Eqs. (2.8)–(2.11) constitute the system of equations we wish to investigate. A similar equation can be derived for the spin–spin correlation function, although we will not consider it here. It should be noted that the presence of a magnetic field modifies the transition rates and the average spin is then coupled to the spin–spin correlation function and the moments then generate a hierarchy of equations. Likewise, a hierarchy of equations results when higher dimensional systems are considered.

We consider two choices of parameters for the impurity model defined by Eq. (2.2). The first choice consists of equal coupling constants J but the spin flip rate α' different for the impurity. The second choice consists of equal α's but J not equal to J'.

It is also necessary to specify the initial conditions. Here, we will consider a localized excitation at the impurity site,

$$\langle s_i \rangle = \delta_{i0} \qquad \text{at} \quad t = 0 \tag{2.13}$$

hence we are perturbing the impurity spin and observing its decay.

3. SOLUTION OF THE EQUATIONS

There are standard techniques which may be used to solve almost any single impurity problem.(9) Given our initial condition we may regard our task as calculating an element of the Green's function for the system. The natural way to solve for this element is to employ the standard, pure, Glauber model as the reference system and treat the impurity as a perturbation. It is convenient to Laplace transform Eq. (2.12) with respect to time, resulting in an infinite set of algebraic equations. In Laplace transform space, the Green's function for the pure system, Eq. (2.12) with all γ's given by Eq. (2.11) and initial condition $\langle S_k \rangle = \delta_{kj}$ at $t = 0$, is

$$G^0_{ij}(z) = \frac{1}{\left[(z+\alpha)^2 - \alpha^2\gamma^2\right]^{1/2}} \left\{ \frac{\alpha\gamma}{(z+\alpha) + \left[(z+a)^2 - \gamma^2\alpha^2\right]^{1/2}} \right\}^{|i-j|} \tag{3.1}$$

where i and j label sites on the chain.(9) We now need to consider the specific perturbation.

Case A

For the case that only the impurity spin–flip rate differs from that of the pure system, the perturbation has the simple form

$$\delta V_{ij} = \delta_{j0}(\alpha' - \alpha)\left[(\gamma/2)(\delta_{j1} + \delta_{j-1}) - \delta_{j0}\right] \tag{3.2}$$

and we may write $G_{ij}(z)$ as

$$G_{ij}(z) = G^0_{ij}(z) + \sum_{k,l} G^0_{ik}(z)\,\delta V_{k,l} G^0_{lj}(z) + \sum_{k,l,m,n} G^0_{ik}(z)\,\delta V_{k,l} G^0_{lm}(z)\,\delta V_{mn} G^0_{nj}(z) + \cdots \tag{3.3}$$

This can be exactly resummed to yield

$$G_{ij}(z) = G^0_{ij}(z) + \frac{G^0_{i0}(z)(\alpha' - \alpha)\left[(\gamma/2)\left(G^0_{1j} + G^0_{-1j}\right)\right] - G_{0j}}{1 - (\alpha' - \alpha)\left[(\gamma/2)\left(G^0_{10} + G^0_{-10}\right) - G^0_{00}\right]} \tag{3.4}$$

and the element we are interested in is simply

$$G_{00}(t) = \frac{G^0_{00}(t)}{1 - (\alpha - \alpha')\left[(\gamma/2)\left(G^0_{10} + G^0_{-10}\right) - G^0_{00}\right]} \tag{3.5}$$

$$= \frac{1}{(\alpha'/\alpha)\left\{\left[(z+\alpha)^2 + \gamma^2\alpha^2\right]^{1/2}\right\} + (1 - (\alpha'/\alpha))z} \tag{3.6}$$

This result is exact. In the next section we discuss this result.

Case B

When the coupling constant J' is not equal to J the analysis becomes more difficult. The same general scheme can be used except now the perturbation is

$$\delta V_{ij} = \alpha\left(\frac{\gamma_2-\gamma}{2}\right)(\delta_{i-1}\delta_{j-2}+\delta_{i+1}\delta_{j+2}) + \alpha\left(\frac{\gamma_1-\gamma}{2}\right)(\delta_{i-1}\delta_{j0}+\delta_{i+1}\delta_{j0}) + \alpha\left(\frac{\gamma_0-\gamma}{2}\right)(\delta_{i0}\delta_{j+1}+\delta_{i0}\delta_{j-1}) \qquad (3.7)$$

where

$$\begin{aligned}\gamma_0 &= \tanh(2\beta J')\\ \gamma_1 &= \tanh[\beta(J+J')] - \tanh[\beta(J-J')]\\ \gamma_2 &= \tanh[\beta(J+J')] + \tanh[\beta(J-J')]\end{aligned} \qquad (3.8)$$

and

$$\gamma = \tanh(2\beta J)$$

To sum the scattering series directly in real space it would be necessary to invert a 5 × 5 matrix. A slightly easier procedure is to consider the Fourier transform

$$G(k,k',z) = \sum_{n,m} e^{ikn} e^{ik'm} G_{mn}(z) \qquad (3.9)$$

which has the following series representation:

$$G(k,k',z) = G^0(k,k',z) + \int\int G^0(k,k_1,z)\,\delta V(k_1,k_2)\,G^0(k_2,k',z)\,dk_1\,dk_2 + \int\int\int\int G^0(k,k_1,z)\,\delta V(k_1k_2)\,G^0(k_2k_3)\,\delta V(k_3k_4)\,G^0(k_4,k',z) \times dk_1\,dk_2\,dk_3\,dk_4 + \cdots \qquad (3.10)$$

where

$$\delta V(k,k') = \alpha(\gamma_1-\gamma)\cos(k) + \alpha(\gamma_0-\gamma)\cos(k') + \alpha(\gamma_2-\gamma)[\cos(k)\cos(2k') - \sin(k)\sin(2k')] \qquad (3.11)$$

In order to sum (3.10) we write $\delta V(k,k')$ as

$$\delta V(k,k') = \sum_{\eta=1}^{4} f_\eta(k) g_\eta(k') \equiv \mathbf{f}\cdot\mathbf{g} \qquad (3.12)$$

where

$$\begin{aligned} f_1 &= \alpha(\gamma_1-\gamma)\cos(k) & g_1 &= 1\\ f_2 &= \alpha(\gamma_0-\gamma) & g_2 &= \cos(k')\\ f_3 &= \alpha(\gamma_2-\gamma)\cos(k) & g_3 &= \cos(2k')\\ f_4 &= -\alpha(\gamma_2-\gamma)\sin(k) & g_4 &= \sin(2k')\end{aligned} \qquad (3.13)$$

and notice that

$$\int\int \delta V(k_1k_2)G^0(k_2k_3)\,\delta V(k_3k_4)\,dk_2\,dk_3$$
$$= \sum_{\eta=1}^{4}\sum_{\mu=1}^{4}\left\{f_\eta(k_1)\left[\int\int g_\eta(k_2)G^0(k_2k_3)f_\mu(k_3)\,dk_2\,dk_3\right]g_\mu(k_4)\right\} \tag{3.14}$$

We define a 4 × 4 matrix

$$A_{\eta\mu}(z) = \int\int g_\eta(k_2)G^0(k_2k_3)f_\mu(k_3)\,dk_2\,dk_3 \tag{3.15}$$

The elements of this matrix will be combinations of G_{ij}^0's. Using Eq. (3.15), Eq. (3.10) becomes

$$G(k,k',z) = G^0(k,k',z) + \int\int G^0(kk_1,z)\mathbf{f}(k_1)\cdot[\mathbf{I} + \mathbf{A} + \mathbf{A}\cdot\mathbf{A} + \cdots]$$
$$\cdot\,\mathbf{g}(k_2)G^0(k_2k',z)\,dk_1\,dk_2$$
$$= G^0(k,k',z) + \int\int G^0(k,k_1,z)\mathbf{f}(k_1)\cdot[\mathbf{I} - \mathbf{A}]^{-1}\cdot\mathbf{g}(k_2)$$
$$\times\, G^0(k_2k',z)\,dk_1\,dk_2 \tag{3.16}$$

The matrix inversion in Eq. (3.16) can be performed analytically. The inverse Fourier transform of Eq. (3.16) can also be performed easily, since all Fourier integrals can be related to G_{ij}^0's. After a considerable amount of algebra, the final expression is found to be

$$G_{00}(z) = \frac{(z+\alpha)(2\gamma-\gamma_2) + \gamma_2\left[(z+\alpha)^2 - \gamma^2\alpha^2\right]^{1/2}}{(z+\alpha)^2[2\gamma-\gamma_2] - \alpha^2\gamma\gamma_1\gamma_0 + \gamma_2(z+\alpha)\left[(z+\alpha)^2-\gamma^2\alpha^2\right]^{1/2}} \tag{3.17}$$

Equations (3.6) and (3.17) are the principal results of the paper. We stress that these are exact results.

One result which can be seen immediately from Eq. (3.17) and (3.8) is that changing the sign of J' does not affect $G_{00}(z)$. This implies that an antiferromagnetic impurity ($J > 0$, $J' < 0$) will relax in exactly the same manner as ferromagnetic impurity ($J > 0, J' > 0$).

4. RESULTS

We are unable to analytically invert the Laplace tranforms in Eqs. (3.6) and (3.17); in order to investigate the temporal behavior we have numerically inverted the Laplace transform using Stehfest's method,(10) to study short and intermediate times, and analytically studied the asymptotic time behavior.

Case A—Numerical Results

Figure 1 shows $G_{00}(t)$ [Eq. (3.6)] for various values of α', where we have scaled the time by α. All curves are for the case $\beta J = 1$. The curve $\alpha' = 1.0$ corresponds to the pure system. Cursory inspection of these curves shows that the major effect of changing the relaxation time is in the initial behavior, where an impurity with a rapid relaxation time (say $\alpha = 5$) decays further before the sluggish bath is able to respond and slow it down. For $\alpha' \ll \alpha$ the curves are flatter, indicating a slower relaxation time.

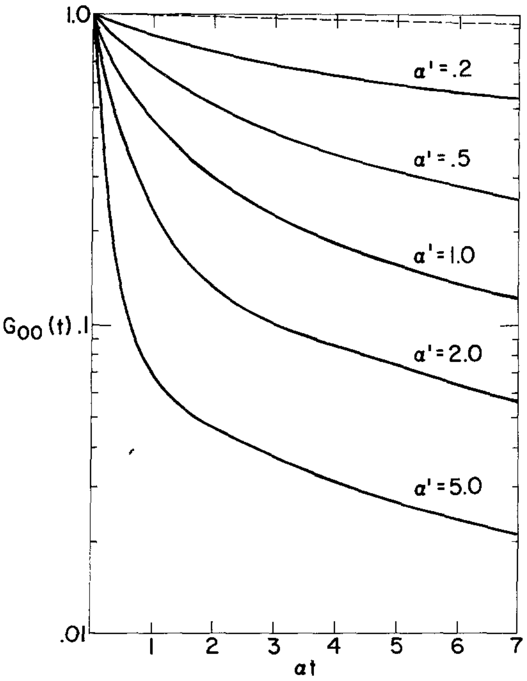

Fig. 1. The decay of the impurity spin for various values of the impurity spin flip rate α'. The dashed line is decaying at the pure system relaxation time $\tau = \alpha^{-1}(1 - \gamma)^{-1}$, for $\beta J = 1$.

Asymptotic Analysis

The asymptotic time behavior of a function can be related to the small-z behavior of its Laplace transform. In general, expressions (3.6) and

(3.17) can have poles and will have branch cuts due to square root. The branch cut can be taken from $z = -\alpha(1+\gamma)$ to $z = -\alpha(1-\gamma)$. The behavior of the function near this cut will dominate asymptotically if there are no poles, or if there are no poles at $z > -\alpha(1-\gamma)$. The expression for the pure Glauber model, Eq. (3.1), has no poles and the branch determines its behavior at long time

$$G_{00}(t) \sim \frac{e^{-\alpha(1-\gamma)t}}{(2\pi\gamma\alpha t)^{1/2}} \tag{4.1}$$

This defines a relaxation time

$$\tau = \alpha^{-1}(1-\gamma)^{-1} \tag{4.2}$$

which goes to infinity as J goes to infinity and γ goes to 1. It is important to note, however, that the system continues to decay due to the $t^{-1/2}$ term. This can be seen clearly in Fig. 1. For $\beta J = 1$, the pure systems relaxation time is $\tau = 109$. The dashed line on Fig. 1 is $f(1) = e^{-t/\tau}$ and is considerably flatter than $\beta J = 1$ (pure system) curve for the times shown on the graph.

Finding the poles of Equation (3.6) reduces to solving a quadratic equation. Care must be taken with the phase of the square root. We find that for $\alpha' > \alpha$ the expression has no poles and the long time behavior is essentially the same as the pure system. The asymptotic relaxation time will be Eq. (4.2). For $\alpha' < \alpha(1-\gamma)$, however, we find a pole appearing at a point on the negative real axis greater than $z = -\alpha(1-\gamma)$ and this pole determines the asymptotic behavior. This is shown in Fig. 2, where we have plotted the asymptotic relaxation time against α'. For $\alpha' \ll \alpha(1-\gamma)$ the relaxation time is

$$\tau = \alpha'^{-1}(1-\gamma^2)^{-1/2} \tag{4.3}$$

For large J, Eqs. (1.1) and (4.3) imply that

$$\tau \simeq \frac{\alpha'^{-1}}{\sqrt{2}}\xi \tag{4.4}$$

The relaxation time, as we decrease α', becomes proportional to the correlation length and not the square of the correlation length squared as in the pure system. It is important to keep in mind that expression (4.4) is valid for fixed values of βJ for asymptotically small values of α'. For fixed α' and βJ increasing, γ will approach 1 and eventually α' will be greater than $\alpha(1-\gamma)$; τ will then approach the pure system result and vanish proportional to the square of correlation length. This agrees with the general analysis of Schneider and Stoll(4) for the behavior of this form of the master equation with a small concentration of impurities. We will discuss this point further in Section 5.

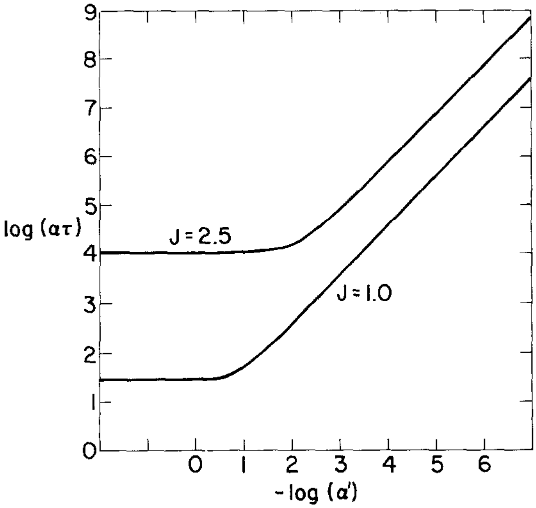

Fig. 2. The asymptotic decay rate for the impurity spin as a function of the impurity spin flip rate α′.

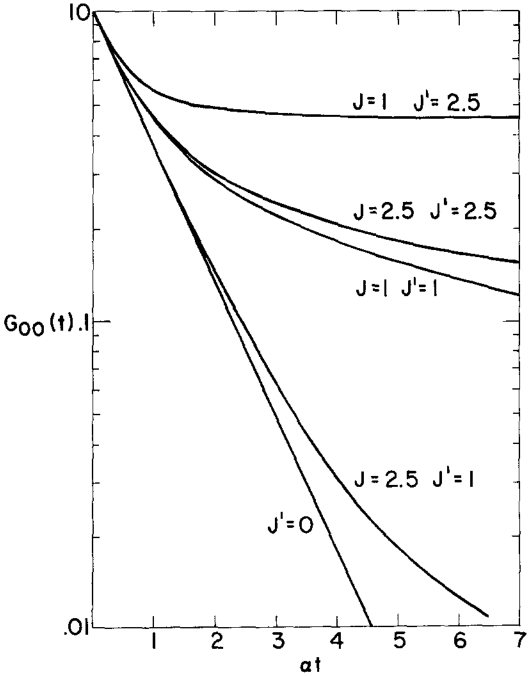

Fig. 3. The decay of the impurity spin for various values of the nearest-neighbor interactions.

Case B—Numerical Results

Sample calculations for $G_{00}(t)$ for various values of βJ and $\beta J'$ are presented in Fig. 3 which reveal several interesting aspects of this system. Even though the behavior of the pure system is not greatly changed between $\beta J = 1$ and $\beta J = 2.5$, we can generate two distinct behaviors when $\beta J = 1$ and $\beta J' = 2.5$ and when $\beta J = 2.5$ and $\beta J' = 1$.

For the intermediate times presented on this graph, the relaxation of an impurity $J' > J$ is slower than even a pure chain with coupling J'. To understand this behavior we need to examine the behavior of γ, γ_0, γ_1, and γ_2 [Eqs. (2.8)–(2.11)]. For $J' > J$ the impurity becomes sluggish because the impurity and its nearest neighbors become a block of three spins weakly coupled to the rest of the chain. In the limit $J' \to \infty$, J finite, these three spins become disconnected from the rest of the chain, and

$$G_{00}(t) = \tfrac{1}{2} + \tfrac{1}{2}e^{-2\alpha t} \tag{4.5}$$

For $J < J'$ the impurity will relax rapidly until the sluggish bath can respond. As J increases, however, it takes longer and longer for the bath to respond and the impurity behaves more like a free spin. Again examining the γ, γ_0, γ_1, and γ_2 we see that the impurity becomes more weakly coupled to the rest of the chain, and in the limit $J \to \infty$, the impurity becomes a free spin, decaying as

$$G_{00}(t) = e^{-\alpha t} \tag{4.6}$$

Asymptotic Analysis

As with case A, we discuss the asymptotic time behavior of expression (3.17) by studying its poles and branch cuts. Again finding the possible poles involves solving a quadratic equation. We find that for $J < J'$, the long time behavior is the same as the pure system. For $J' > J$, there is a different, slower relaxation time. These results are shown in Fig. 4, where the relaxation time is plotted againt $\beta J'$ for various values of βJ. In the limit that $\beta J' \gg \beta J$, the relaxation time approaches

$$\tau = \alpha^{-1}e^{-2\beta J'} \tag{4.7}$$

as clearly seen in Fig. 4. This result is the decay rate for an isolated three spin block with coupling constant J'. We see that if $J' > J$ and the temperature of the system is lowered, β will increase and the impurity will eventually have the relaxation time given in Eq. (4.7). This result is independent of J and is hence not directly related to the correlation length of the system.

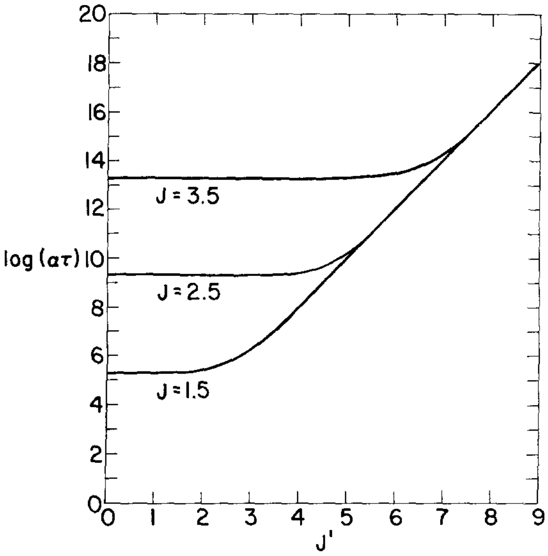

Fig. 4. The asymptotic decay rate for the impurity spin as a function of the impurity spin's nearest-neighbor coupling.

5. DISCUSSION

The general conclusion from studying this model is that as the bulk system is critically slowed a separation of time scales occurs and the bulk's influence on the impurity correspondingly decreases. This simple model shows a variety of behaviors, depending on the nature of the impurity. The case of differing coupling constants demonstrates clearly the local nature of the decay. If the impurity is less strongly coupled ($J' < J$), driving the bulk toward "freezing" allows the spin to relax unhindered by the bulk for longer periods of time. If the impurity is more strongly coupled ($J' > J$), a small block of spins near it becomes independent of bulk as the bulk slows down. There is also a separation of length scales occurring that frees the local impurity.

Certain peculiarities must be expected from the one-dimensional character of the model. In relation to this, an additional comment on the work of Schneider and Stoll(4) is in order. Their results are basically for higher-dimensional systems. They assume that the impurity spin flipping is an activated process

$$\alpha' = \alpha e^{-\beta\Delta E} \tag{5.1}$$

where α is the temperature-independent spin-flip rate for the bulk. They also assume a nonzero critical temperature, which implies that α' is also nonzero at the critical point. If we were to assume this form for α' in the one-dimensional model, the asymptotic time behavior of the system as $T \to 0$ will depend on ΔE. Specifically, by analyzing the poles of Eq. (3.6) we find that if $\Delta E < 2J$, the system will decay asymptotically in the same manner as the case of fixed α' and βJ increasing, and $\tau \propto \xi^2$. If $E > 2J$, the system behaves as the $\alpha \gg \alpha'$, fixed βJ case, and $\tau \propto \xi$. If α' did not vanish at the critical temperature, this behavior would not occur.

The Glauber model has been used to model many different systems and in many of these systems impurities can be important. For example, in modeling cooperative effects in enzymatic reactions, it is not unreasonable to model a single different enzyme as an impurity. Unfortunately, in many cases the resulting spin system must be in an external field, a complication that does not allow any of the Glauber models to be solved exactly.

In closing, we return to our original interest, chemical process in "critical" situations. In the introduction we discussed the type of critical behavior for which this would be a relevant model for the dynamics. In addition, the absence of an external magnetic field in our calculations means the model can only be taken as an analogy to an isothermic reaction and to a solvent with no chemical potential difference between its two states. The interaction energies between the reactant and solvent are also restricted. To avoid introducing an external field, it is necessary that the energy of one state of the reactant interacting with one state of a neighboring solvent molecule be equal to the energy of the other state of the reactant interacting with the other state of the solvent. Although the direct analogy is to an extremely limited type of chemical reaction and solvent system, within these limitations, the conclusion drawn for our model is that the bulk solvent has *less* effect on the rate of the reaction as the system is critically slowed.

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REFERENCES

1. R. J. Glauber as quoted by H. E. Stanley (personal communication).
2. R. J. Glauber, *J. Math. Phys.* **4**:294 (1963).
3. D. Dhar and M. Barma, *J. Stat. Phys.* **22**:259 (1977).
4. T. Schneider and E. Stoll, *Phys. Rev. B* **16**:2220 (1977).
5. N. S. Gael, *Biopolymers* **6**:55 (1968).
6. T. L. Hill, *Proc. Nat. Acad. Sci.* **74**:3632 (1977).

7. M. Gitterman and V. Steinberg, *J. Chem. Phys.* **69**:2763 (1978).
8. (a) M. Suzuki and R. Kubo, *J. Phys. Soc. Jpn* **24**:51 (1968). (b) B. U. Felderhof, *Rep. Math. Phys.* **1**:215 (1971). (c) K. Kawasaki in *Phase Transitions and Critical Phenomena*, Chap. 11, C. Domb and M. S. Green, eds. (Academic Press, New York, 1972).
9. For example, see E. N. Economou, *Green's Functions in Quantum Physics*, (Springer Verlag, Berlin, 1979).
10. H. Stehfest, *Comm. A.C.M.* **13**, 47, 624 (1970).