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Dynamics of the Generalized Glauber–Ising Chain in a Magnetic Field

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A one-dimensional kinetic Ising model with nearest neighbor interaction J and magnetic field $H \geqslant 0$ is treated in both linear and nonlinear response, using the most general single spin-flip transition probabilities that depend on nearest neighbor states only. The dynamics is reformulated in terms of kinetic equations for the concentration $n_l^+(t)$ $[n_l^-(t)]$ of clusters containing l up- [or down-] spins, which is exact in the homogeneous case. The initial relaxation time τ^* of the magnetization is obtained rigorously for arbitrary J, H, and temperature T. The relaxation function is found by numerical integration for $J/T \lessgtr 2$. It is shown that "coagulation" of minus-clusters becomes negligible for both J/T and H/T large, and the resulting set of equations is solved exactly in terms of an eigenvalue problem. A perturbation theory is developed to take into account the neglected coagulation terms. The relaxation function is found to be non-Lorentzian in general, in contrast to the Glauber results at $H = 0$, which are recovered as a special case. In addition, nonlinear and linear relaxation functions differ for $H \neq 0$. Consequences for the application to biopolymers are briefly mentioned.

KEY WORDS: Ising model; master equation; clusters; nonlinear response; relaxation functions; biopolymers.

1. INTRODUCTION

In the stochastic Ising models$^{(1-16)}$ Ising spins on a lattice are in contact with a heat bath which induces random flips of the spins from one state to another. This rather simple model for the irreversible statistical mechanics of a cooperative system has found much interest, because: (i) it can be solved exactly for the case of zero magnetic field and a certain choice of transition probability W on a one-dimensional lattice,$^{(1,3-5)}$ and both

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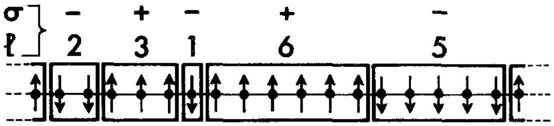


Fig. 1. Each state of an Ising chain is characterized by a certain sequence of clusters $\{l, \sigma\}$.

linear$^{(1,3)}$ and nonlinear$^{(5)}$ response functions have been obtained; (ii) a variety of approximate techniques can be worked out for these models and thus tested (e.g., the dynamic mean-field$^{(2,3)}$ and Bethe approximations$^{(9)}$ or other decouplings of the equations of motion of correlation functions,$^{(10,11)}$ "cluster-dynamics" approaches,$^{(8,14)}$ Monte Carlo calculations,$^{(13)}$ high-temperature series expansions,$^{(15,16)}$ etc.); (iii) the model can be used to approximate the kinetics of anisotropic magnets,$^{(12,13)}$ alloys undergoing order–disorder transitions,$^{(17,18)}$ and structural transitions$^{(19)}$; (iv) finally, the one-dimensional version can be used to approximately describe$^{(10,11)}$ the kinetics of helix-coil transitions$^{(20,21)}$ in biopolymers.

Now, unfortunately, for this last application the exactly solved case is not sufficient since one would require both more general transition probabilities and nonzero field.$^{(10,11,21)}$ The validity of approximations$^{(2,3,9-11)}$ is uncertain and even doubtful because of the fact that mean-field-like factorization approximations are known to become worse, the lower is the dimensionality of the system.$^{(22)}$ Exact results of Hilhorst$^{(8)}$,[2] also concern a too restricted choice of transition probability. In the present paper we develop an approach$^{(23)}$,[3] by which the relaxation can be treated for arbitrary values of the parameters and general transition probabilities. As in Refs. 6 and 8, it is based on the use of the concentrations n_l^σ of "clusters" of l up ($\sigma = 1$) or down ($\sigma = -1$) spins in thermal equilibrium (Fig. 1) obtained exactly by Felderhof.$^{(25)}$ In Section 2, we reformulate the master equation in terms of time-dependent concentrations of these clusters $n_l^\sigma(t)$. In Section 3 the initial relaxation time τ^* commonly used in biochemical work$^{(10,21)}$ is obtained rigorously. Section 4 discusses numerical solutions of our set of kinetic equations, while in Section 5 an approximation is treated where (for $H/T > 1$) coagulation of clusters of up-spins is neglected. The resulting relaxation functions can be obtained analytically. A perturbation theory is developed by which the neglected terms can be taken into account, and first-order corrections are obtained again analytically. In Section 6 we briefly discuss the relevance of our results to biopolymers, but defer a more detailed comparison of our results with experiments and with previous approximations$^{(10)}$ to a separate publication.$^{(26)}$

[2] An algebraic error in Ref. 8 is pointed out in Section 5.

[3] Some of our results are reported briefly in Ref. 24.

2. KINETIC ISING MODEL AND CLUSTER DYNAMICS

The single spin-flip kinetic Ising model is defined in terms of a Markovian master equation for the probability distribution $P(\mu_1,\dots,\mu_N,t)$ for the spins $\{\mu_i = \pm 1\}$,⁽¹²⁾

$$\begin{aligned}\frac{d}{dt}P(\mu_1,\dots,\mu_N,t) = &-\sum_{j=1}^{N} W(\mu_j \to -\mu_j)P(\mu_1,\dots,\mu_j,\dots,\mu_N,t)\\ &+\sum_{j=1}^{N} W(-\mu_j \to \mu_j)P(\mu_1,\dots,-\mu_j,\dots,\mu_N,t)\end{aligned} \tag{1}$$

where the transition probabilities W satisfy the detailed balance condition with the equilibrium distribution $P_0(\mu_1,\dots,\mu_N)$,

$$W(\mu_j \to -\mu_j)P_0(\mu_1,\dots,\mu_j,\dots,\mu_N) = W(-\mu_j \to \mu_i)P_0(\mu_1,\dots,\mu_j,\dots,\mu_N) \tag{2}$$

and are otherwise arbitrary. P_0 can be expressed in terms of the Hamiltonian $\mathscr{H}$ as $P_0 = (1/Z)\exp(-\mathscr{H}/T)$, where $k_B = 1$, Z is the partition function, and

$$\mathscr{H} = -(J/2)\sum_{i=1}^{N}\mu_i(\mu_{i+1}+\mu_{i-1}) - H\sum_{i=1}^{N}\mu_i \tag{3}$$

and we make the system translationally invariant (disregarding end effects in the chain) by the periodicity condition

$$\mu_{N+1} = \mu_1, \qquad \mu_0 = \mu_N, \qquad N \to \infty \tag{4}$$

The transition probability describes the random flipping of the spins induced by the heat bath. Physically, it seems reasonable to assume that the coupling that produces these flips is a local interaction, and thus the flip rate W should not depend on the global state of the system but only on the local environment of the considered spin. Since derivations of the master equation (1) from more microscopic considerations are available only for rather special cases,^(27–29) we tentatively assume that W depends on the state of the nearest neighbors only. Since right and left neighbors are equivalent, there exist then only six different rates $W_0{}^+$, $W_0{}^-$, $W_-{}^+$, $W_-{}^-$, $W_+{}^+$, and $W_+{}^-$ (cf. Fig. 2), of which only three are independent because of Eq. (2), which gives

$$\begin{aligned} W_0{}^+/W_0{}^- &= e^{-2H/T},\\ W_-{}^+/W_-{}^- &= e^{-(4J+2H)/T},\\ W_+{}^+/W_+{}^- &= e^{+(4J-2H)/T}\end{aligned} \tag{5}$$

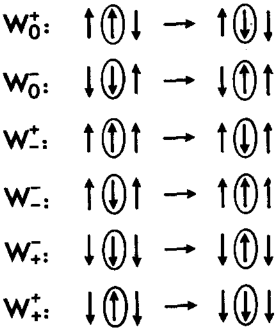


Fig. 2. Transition probabilities w that describe the flipping of the encircled spin.

W_0^+ (W_0^-) is the probability that an up-spin (down-spin) at the end of an l-cluster ($l > 2$) is flipped per unit time, W_-^+ (W_-^-) is the probability that a $(1, -)$-cluster is created [destroyed], and W_+^+ (W_+^-) is the probability that a $(1, +)$-cluster is created (destroyed).

The standard Glauber model$^{(1)}$ is a special case of Eq. (5), with

$$\begin{aligned} W_0^+ &= [1 - \tanh(H/T)]/2\tau_\infty \\ W_-^+ &= \left[1 - \tanh\left(\frac{H + 2J}{T}\right)\right]\Big/2\tau_\infty, \\ W_+^+ &= \left[1 - \tanh\left(\frac{H - 2J}{T}\right)\right]\Big/2\tau_\infty \end{aligned} \tag{6}$$

i.e., instead of three independent rate factors W_0^+, W_-^+, and W_+^+, one has only one rate factor τ_∞^{-1}.

Now we make use of the fact that each state of the Ising chain is uniquely specified in terms of the sequence of clusters $\{(l, \sigma)\}$. Consider, e.g., a part of the sequence $(l', -)$, $(l, +)$, $(l'', -)$. The contribution of the spins in the l-cluster to the energy of the system does not depend on the magnitude of l' and l'' (by definition a cluster of up-spins must have neighboring clusters of down-spins of some size). Therefore it is clear that in thermal equilibrium on the average there is no correlation between the lengths of neighboring clusters in the chain, i.e., in a translationally invariant system the probability that an $(l'', -)$-cluster follows an $(l, +)$-cluster is equal to its relative probability $f_{l''}^-$, where

$$f_{l'}^\sigma = n_{l'}^\sigma / n, \qquad n = \sum_{l=1}^{\infty} n_l^+ = \sum_{l=1}^{\infty} n_l^- \tag{7}$$

Suppose now we consider nonequilibrium relaxation processes where the system is kept in thermal equilibrium (characterized by H_0, T_0) for times $t < 0$, while at $t = 0$ the external conditions are changed such that a new equilibrium (characterized by H, T) has to be established. Clearly, the dynamics defined by Eqs. (1)–(5) should not create any correlations in the lengths of neighboring clusters, i.e., the probability that an (l'', $-$)-cluster follows an (l, $+$)-cluster is still given by its relative probability $f_{l''}^{-}(t)$, which now depends on time:

$$f_{l'}^{\sigma}(t) = n_{l'}^{\sigma}(t)/n(t), \qquad n(t) = \sum_{l=1}^{\infty} n_l{}^{+}(t) = \sum_{l=1}^{\infty} n_l{}^{-}(t) \tag{8}$$

Thus the microscopic information contained in the specific cluster sequence is unnecessary for our purposes, and it suffices to describe the system by the set $\{n_l{}^{+}(t), n_l{}^{-}(t)\}$ (which we abbreviate by $\{n\}$) at each time t. Equation (1) can then be replaced by the "coarse-grained"$^{(6)}$ master equation valid for a large but finite chain:

$$\begin{aligned}\frac{d}{dt} P(\{n\}, t) = &-\sum_{\{n'\}} W(\{n\} \to \{n'\}) P(\{n\}, t)\\ &+ \sum_{\{n'\}} W(\{n'\} \to \{n\}) P(\{n'\}, t)\end{aligned} \tag{9}$$

The price which is paid for this coarse-graining is that it is approximate if the initial state contains correlations in the lengths of neighboring clusters; but we think it is still exact for the description of the relaxation from one spatially uniform state to another. However, in the following we will not be concerned with the solution of the full Eq. (9), but only its first moment:

$$\begin{aligned}\frac{d}{dt} n_l{}^{+}(t) = {}& 2 \sum_{k=1}^{N-l} [W_0{}^{-} f_{k+1}^{-}(t) n_{l-1}^{+}(t) - W_0{}^{+} f_k{}^{-}(t) n_l{}^{+}(t)]_{l \geqslant 2}\\ &+ 2 \sum_{k=1}^{N-l-1} [W_0{}^{+} f_k{}^{-}(t) n_{l+1}^{+}(t) - W_0{}^{-} f_{k+1}^{-}(t) n_l{}^{+}(t)]_{l \geqslant 1}\\ &+ 2 \sum_{k=1}^{N-l-1} [W_-{}^{+} n_{l+k+1}^{+}(t) - W_-{}^{-} f_k{}^{+}(t) f_1{}^{-}(t) n_l{}^{+}(t)]_{l \geqslant 1}\\ &+ \sum_{k=1}^{l-2} [W_-{}^{-} f_k{}^{+}(t) f_1{}^{-}(t) n_{l-k-1}^{+}(t) - W_-{}^{+} n_l{}^{+}(t)]_{l \geqslant 3}\\ &+ \sum_{m=1}^{N-2} \sum_{k=1}^{N-m-1} [W_+{}^{-} n_{m+k+1}^{-}(t) - W_+{}^{+} f_k{}^{-}(t) n_1{}^{+}(t) f_m{}^{-}(t)]_{l=1}\end{aligned} \tag{10}$$

The equation for $n_l{}^{-}(t)$ follows from Eq. (10) by changing the signs of all superscripts $+$, $-$ (and also the signs of the subscripts in the W's). Equation

(10) can be understood immediately from Fig. 2 by systematically enumerating all possibilities; the factor 2 in the first three lines accounts for the fact that reactions occurring at the end of a cluster can occur on both ends of it. The index on the brackets [$\cdots$] shows for which cluster sizes the corresponding contribution has to be taken into account. In thermal equilibrium each bracket [$\cdots$] vanishes individually because of detailed balance. In fact, the resulting equations can be used to construct the thermal equilibrium values for the n_l^σ, which agree with those found by Felderhof,(25)

$$\begin{aligned} n_l^\sigma &= n \frac{1 - q_\sigma}{1 - q_\sigma^N} q_\sigma^{l-1} \\ q_\sigma &= \frac{\exp(\sigma H/T)}{\cosh(H/T) + [\sinh^2(H/T) + \exp(-4J/T)]^{1/2}} \end{aligned} \tag{11}$$

Note that $\xi_\sigma = (1 - q_\sigma)^{-1}$ is the average length of the σ-clusters (for $H = 0$, $\xi_+ = \xi_- = \xi$ is simply the correlation length).

Eq. (10) is the first central result of our paper, on which all subsequent discussion is based. In a previous work Felderhof(6) gave a general expression but did not explicitly give the proper summation limits nor did he include the last line of Eq. (10). Hilhorst's work(8) was concerned with the special case $W_-^{\,-} = W_-^{\,+} = W_+^{\,-} = W_+^{\,+} = 0$ only. Clearly, a complete solution of Eq. (10) is very difficult due to the nonlinear terms.

In the following, it will be convenient to use a vector notation,

$$|n^\sigma(t)\rangle = \{n_1^\sigma(t), n_2^\sigma(t), \ldots\}, \qquad \langle l|a\rangle \equiv \sum_{l=1}^{\infty} l a_l \tag{12}$$

for arbitrary functions a_l of the cluster length index l. Then Eq. (10) is more compactly rewritten as

$$(d/dt)|n^\sigma(t)\rangle = -\mathbf{L}^\sigma(t)|n^\sigma(t)\rangle \tag{13}$$

where the "Liouville operator" $\mathbf{L}^\sigma(t)$ can be conveniently expressed in terms of its matrix elements,(23) while the cluster density $n(t)$ changes only due to the "nucleation rate" $\Gamma(t)$

$$(d/dt)n(t) = \Gamma(t)n(t), \qquad \Gamma(t) = \Gamma^-(t) - \Gamma^+(t) \tag{14}$$

with

$$\Gamma^\sigma(t) = \sigma W_\sigma^{\,\sigma} f_1^{\,\sigma}(t) - \sigma W_{\bar\sigma}^{\,-\sigma}[f_{\bar 1}^{\,-\sigma}(t) - 2 + \langle l|f^{-\sigma}(t)\rangle] \tag{15}$$

where $|f^\sigma(t)\rangle = \{f_1^\sigma(t), f_2^\sigma(t), \ldots\}$. The $\Gamma^\sigma(t)$ describes the rate at which $(1, \sigma)$-clusters are formed per unit time.

We now introduce the function $\Phi_A^{\Delta e}(t)$ to describe the relaxation of the quantity A after a change Δe of an external parameter e (temperature T, field H, etc.)$^{(16,30)}$

$$\Phi_A^{\Delta e}(t) = [\langle A(t)\rangle - \langle A(\infty)\rangle]/[\langle A(0)\rangle - \langle A(\infty)\rangle] \tag{16}$$

For $\Delta e \to 0$, Eq. (16) reduces to an ordinary linear response-function, which is related to dynamic correlation functions via standard fluctuation-dissipation relations.$^{(12)}$ We use Eq. (16) since we wish to include explicitly the case of highly nonlinear relaxation, where Δe is not small (nonlinear relaxation is important for the application to biopolymers, where frequently "temperature jump" methods are used$^{(10,22)}$). The quantities A that are of interest here are magnetization/spin

$$\langle \mu(t)\rangle = \langle l|n^+(t)\rangle - \langle l|n^-(t)\rangle = 1 - 2\langle l|n^-(t)\rangle \tag{17}$$

and internal energy/spin $\langle \epsilon(t)\rangle$, where one makes use of the fact that the contribution of an (l, σ)-cluster to the total energy is $\epsilon_l^\sigma = -(l-2)J - \sigma Hl$, and hence

$$\langle \epsilon(t)\rangle = \langle \epsilon^+|n^+(t)\rangle + \langle \epsilon^-|n^-(t)\rangle = -J + 4Jn(t) - H\langle \mu(t)\rangle \tag{18}$$

In Eqs. (17) and (18) we have made use of the relation $\langle l|n^+(t)\rangle + \langle l|n^-(t)\rangle = 1$, which expresses the fact that each spin must belong to some cluster. The order-parameter relaxation time τ and the associated initial relaxation time τ^* are then defined as

$$\tau = \int_0^\infty dt\, \Phi_\mu^{\Delta e}(t), \qquad \tau^* = -\left\{\frac{d}{dt}\,\Phi_\mu^{\Delta e}(t)\Big|_{t=0}\right\}^{-1} \tag{19}$$

If the relaxation is "monodispersive" and hence Lorentzian (i.e., $\Phi_\mu^{\Delta e}(t) = e^{-t/\tau}$), $\tau^* = \tau$, as occurs in the Glauber model for $H = 0$.$^{(1)}$ In the case of polydispersive relaxation, $\tau^*/\tau \neq 1$, this ratio hence can be taken to measure the degree of "polydispersiveness" (i.e., the extent to which a whole spectrum of relaxation times contribute). There has been some discussion in the literature$^{(10,31)}$ of what τ^*/τ is for $H \neq 0$ and other choices of transition probabilities, but no completely conclusive answers have been obtained. Clarification of this question is one of the aims of the present paper.

3. BEHAVIOR OF THE INITIAL RELAXATION TIME τ^*

From Eqs. (13), (16), (17), and (19) we immediately obtain

$$\frac{1}{\tau^*} = -\frac{2}{\langle \mu(0)\rangle - \langle \mu(\infty)\rangle}\langle l|\mathbf{L}^-(0)|n^-(0)\rangle \tag{20}$$

Using for the initial values $|n^-(0)\rangle$ cluster concentrations appropriate for thermal equilibrium T_0, H_0 [and hence Eq. (11)], it is possible to evaluate Eq. (20) exactly, both in the case of linear and nonlinear response. From Eqs. (10) and (13) one first obtains, suitably rearranging the sums,(23)

$$
\begin{aligned}
&\frac{1}{\rho(0)}\langle l|\mathbf{L}^{-}(0)|n^{-}(0)\rangle \\
&\quad = 2\sum_{l=1}^{N}\sum_{k=1}^{N-l-1}(W_0{}^{+}f_{k+1}^{+}f_l{}^{-} - W_0{}^{-}f_k{}^{+}f_{l+1}^{-}) \\
&\quad\quad + \sum_{l=1}^{N-2}\sum_{k=1}^{N-l-1}(W_-{}^{+}f_{l+k+1}^{+} - W_-{}^{-}f_k{}^{+}f_1{}^{-}f_l{}^{+}) \\
&\quad\quad + 2\sum_{l=1}^{N-2} l \sum_{k=1}^{N-l-1}(W_+{}^{-}f_{l+k+1}^{-} - W_+{}^{+}f_k{}^{-}f_1{}^{-}f_l{}^{-})
\end{aligned}
\tag{21}
$$

where the $f_m{}^{\sigma}$ refer to the initial thermal equilibrium at H_0, T_0. Information on the final equilibrium is contained in the W's. Using Eqs. (7) and (11) and evaluating the resulting geometrical series, one obtains (see Ref. 23 for details of the tedious but straightforward algebra) for $N \to \infty$

$$\frac{1}{\tau^*} = \frac{2n(0)}{\langle\mu(0)\rangle - \langle\mu(\infty)\rangle}[2(W_0{}^{+}q_+ - W_0{}^{-}q_-) + \Gamma^{+}(0) + \Gamma^{-}(0)] \tag{22}$$

with

$$\Gamma^{\sigma}(0) = \sigma W_{\sigma}{}^{\sigma}(1 - q_{\sigma}) - \sigma W_{\sigma}^{-\sigma}(q_{-\sigma})^2/(1 - q_{-\sigma}) \tag{23}$$

and the q_+, q_- refer to the initial thermal equilibrium. Exact expressions of τ^* for N finite are more complicated and can be found in Ref. 23. Making use of de l'Hospital's rule, Eq. (22) can be used also for the linear response. One obtains

$$\left(\frac{1}{\tau^*}\right)_{\text{lin}} = \frac{(2 - q_+ - q_-)^2}{q_+ + q_-}[2W_0{}^{+}q_+ + W_-{}^{-}(1 - q_-) + W_+{}^{+}(1 - q_+)] \tag{24}$$

Using the Glauber(1) choice of transition probabilities, Eq. (6), one finds from Eq. (11) for $H = 0$ that $\tau^* = \tau_\infty/[1 - \tanh(2J/T)]$, i.e., Glauber's result,(1) as expected. Furthermore, it follows from Eq. (24) that the contribution proportional to $W_0{}^{+}$ [i.e., the terms describing cluster growth and shrinking in Eq. (10)] is dominant at low temperatures, $\tau^*/\tau_\infty \approx \exp(4J/T)/2$. The contribution of nucleation of (1, −)-clusters (proportional to $W_-{}^{-}$) as well as of (1, +)-clusters (proportional to $W_+{}^{+}$) is negligible, i.e., one obtains corrections of order $e^{-3J/T}$. Hilhorst,(8) who omitted the $W_-{}^{-}$ and $W_+{}^{+}$ from the very beginning, obtained a different amplitude factor $[\tau^*/\tau_\infty = 3\exp(4J/T)/2]$ due to an algebraic error.(23)

For nonzero fields the situation is different even if one chooses the Glauber transition probabilities: The contribution of growing and shrinking of clusters ($W_0{}^+$) to the rate ($1/\tau^*$) at low temperatures ($T/J \ll 1$) is negligible [i.e., $\sim\exp(-2H/T)/\tau_\infty$] in comparison with the nucleation of (1, $-$)-clusters (which gives a contribution $\sim 1/\tau_\infty$), while the nucleation of (1, $+$)-clusters is of order $\exp[-(4J + 2H)/T]/\tau_\infty$ for $H < 2J$ or $\exp(-4H/T)/\tau_\infty$ for $H > 2J$. Hence the Hilhorst model(8) does not constitute a reasonable approximation to the Glauber model except for $H/T \to 0$. This failure has a simple physical explanation: For H/T large, the magnetization is close to unity, and then the cluster density $n(t)$ is very low, the chain contains only few (and small) (l, $-$)-clusters and at the same time few (but large) (l, $+$)-clusters. Since a growing–shrinking event can occur only at the two sites at the end of such an (l, $+$)-cluster, while nucleation of (1, $-$)-clusters can occur at any of the $l - 2$ sites in the interior of the cluster, it is clear that these nucleation events must be the dominating process. This observation of very different rates for the various processes will be the starting point of our perturbation method developed in Section 5.

Figure 3 illustrates the behavior of τ^*/τ_∞ as a function of H/T for larger values of T/J. While linear and nonlinear relaxation times agree for $H = 0$ (as expected from Refs. 1 and 5), this is no longer true for $H \neq 0$: As expected, the nonlinear relaxation is now quicker than the linear one. A similar difference also has been detected in other models.(16,19,32) For $H/T \gg 1$, τ^* approaches τ_∞ for all J/T, as expected since then the magnetization saturates and always the nucleation of (1, $-$)-clusters and the reverse process become the dominant mechanism. Finally, we note that Eq. (24) has been obtained by a completely different method by Schwarz.(33)

For the Glauber(1) choice of transition probabilities the relaxation is Lorentzian for $H = 0$ and hence it is reasonable to approximate it by a Lorentzian also for small but nonzero H/T, i.e., $\Phi_\mu^{\Delta e}(t) = \exp(-t/\tau^*)$, with τ^* given in Eq. (22) or (24). Our numerical treatment (Section 4) suggests

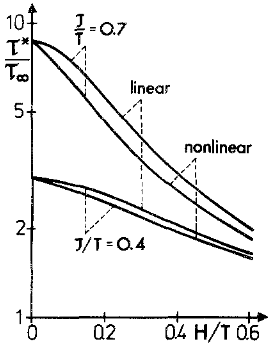


Fig. 3. Initial relaxation time τ^* of the Glauber model plotted vs. field at two temperatures for the cases of linear response ($\Delta H \to 0$) and nonlinear response ($\Delta H/T = 5.0$).

that the same approximation is accurate also for $T/J > 2$ and arbitrary H/T. Of course, for $T/J \gg 1$ one does expect a Lorentzian relaxation even for arbitrary choices of the transition probabilities, since then the relaxation of the spins is not much affected by their interactions; one rather has a relaxation of independent spins, which is of course exponential, as a treatment based directly on Eq. (1) shows.

4. NUMERICAL INTEGRATION OF THE EQUATIONS OF MOTION FOR THE CLUSTER CONCENTRATIONS

In principle, it is a straightforward matter to integrate Eq. (10) numerically on a computer for not too large N, using the n_l^σ of Eq. (11) for the appropriate T_0, H_0 as starting values. However, there is little interest in the properties of kinetic Ising chains for finite N; in the case of periodic boundary conditions one is rather interested in $N \to \infty$. Equation (10) approximates this case only if the $n_l^\sigma(t)$ are negligibly small if l is of the order of N. A necessary condition is thus $\xi_+ \ll N$, $\xi_- \ll N$ for both the initial and the final states, or, more precisely [cf. Eq. (11)]

$$[q_\sigma(t=0)]^N \ll 1, \qquad [q_\sigma(t=\infty)]^N \ll 1 \tag{25}$$

since then the cluster distributions of both the initial and the final states deviate negligibly from the distribution in the thermodynamic limit. Since the normalized cluster concentrations $[n_l^\sigma(t) - n_l^\sigma(\infty)]/[n_l^\sigma(0) - n_l^\sigma(\infty)]$ can be shown^(23) to decay to zero monotonically, finite-size effects then are negligible throughout the relaxation process.

From Eqs. (11) and (25) it follows that for $J/T = 1.5$ and $H/T = 0.085$ one needs already an N as large as 1000 (for higher temperatures and/or smaller fields smaller values of N are sufficient). Hence the practical difficulties are comparable to that of the "molecular dynamics" method (see Adler^(34) for a review). Several integration routines have been tested. In our case the Adam extrapolation formula^(35)

$$n_l^\sigma(t+\Delta t) = n_l^\sigma(t) + \Delta t\left[\frac{23}{12}\frac{d}{dt}n_l^\sigma(t)\bigg|_t - \frac{16}{12}\frac{d}{dt}n_l^\sigma(t)\bigg|_{t-\Delta t} + \frac{5}{12}\frac{d}{dt}n_l^\sigma(t)\bigg|_{t-2\Delta t}\right] \tag{26}$$

gave the most satisfactory results. For instance, at $J/T = 1.5$ an integration interval $\Delta t = 0.1\tau_\infty$ was sufficient to keep the error of all $n_l^\sigma(t)$ smaller than 1%. Figures 4–6 give some typical results for the case of the Glauber^(1) transition probabilities, Eq. (6). Figure 4 collects some calculations in the high-temperature region ($J/T < 0.5$). At $J/T = 0.1$, linear ($\Delta T \to 0$) and

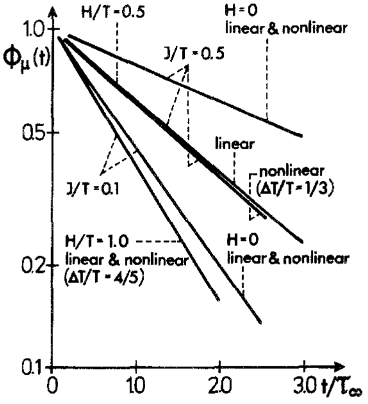


Fig. 4. Linear and nonlinear relaxation functions of the order parameter plotted vs. time after a jump ΔT of temperature for various temperatures and fields.

nonlinear relaxation functions coincide with each other both for zero field (in which case the results agree precisely with those of Glauber) and for nonzero field, and are simple Lorentzians within our accuracy. The same is true for $J/T = 0.5$ in zero field, while there a slightly different result is obtained for nonzero field: In the nonlinear case the order parameter relaxes slightly quicker than in the linear case, which is still Lorentzian. The asymptotic relaxation time (i.e., the slope of the relaxation function in the semilog plot, Fig. 4, for $t \to \infty$) is the same, of course, as in the linear case, and thus the relaxation function is slightly non-Lorentzian. Figures 5 and 6 show that these deviations from Lorentzian behavior become more pronounced at low temperatures, and now show up in the linear relaxation function as well, if H/T differs from zero appreciably. Then also the difference between the linear and nonlinear case is rather pronounced. For zero field, however, the results always agree precisely with that of Glauber,(1) and hence yield coincidence of linear and nonlinear functions and Lorentzian relaxation.

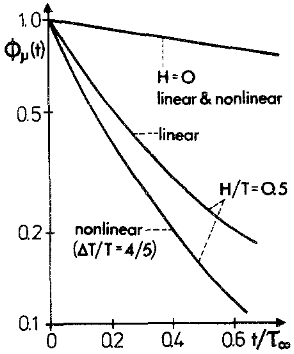


Fig. 5. Semilog plot of linear and nonlinear relaxation functions at $J/T = 1.0$ and two values of the field.

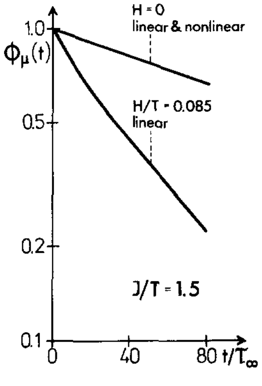


Fig. 6. Semilog plot of relaxation functions at $J/T = 1.5$ and two values of the field.

A comparison of the time scales of Figs. 4–6 also reveals the "critical slowing down" of the relaxation as J/T becomes large. Since ξ (or ξ^+) becomes large at the same time, it would be hard to proceed to substantially lower temperatures than those shown. The temperature range shown does comprise, however, the temperatures that are of interest for applications to biopolymers.(10,20,21,26) In this case the Glauber transition probabilities are perhaps not appropriate. But calculations similar to those shown in Figs. 4–6 but with other choices of the W's are in principle straightforward by our method (some examples can be found in Ref. 26).

5. PERTURBATION METHOD FOR THE RELAXATION IN STATES CLOSE TO THE FULLY ORDERED STATE

5.1. The Zeroth Approximation

If the magnetization of the system is close to unity, the configurations of the system contain large $\{l, +\}$-clusters but only rather small $\{l, -\}$-clusters: hence the nucleation rate of $\{1, +\}$-clusters (which can take place at the interior sites of the $\{l, -\}$-clusters only) is negligibly small in comparison with the nucleation rate of $\{1, -\}$-clusters (Section 3). This fact suggests that we use a "zeroth approximation" where nucleation of $\{1, +\}$-clusters is neglected. We start from Eqs. (13) and (14), which are rewritten in matrix notation ($l, k = 1,\ldots, N$)

$$\begin{aligned} \frac{d}{dt}|f^\sigma(t)\rangle &= -\{\mathbf{L}^\sigma(t) + \delta_{lk}\Gamma(t)\}|f(t)\rangle \\ \mathbf{L}^\sigma(t) &= \{\mathbf{L}^\sigma_{gs}(t) + \mathbf{L}_n^{-\sigma}(t) + \sigma\delta_{l1}\delta_{1k}\Gamma^\sigma(t)/f_1{}^\sigma(t)\} \end{aligned} \tag{27}$$

where the matrix $L^\sigma_{gs}(t)$ describes the growing and shrinking of clusters, $L_n^{-\sigma}(t)$ describes nucleation of $(1, -\sigma)$-clusters, and the matrix $[\sigma\delta_{l1}\delta_{1k}\Gamma^\sigma(t)/f_1{}^\sigma(t)\}$ (with only one nonzero matrix element) describes nucleation of $(1,\sigma)$-clusters. From Eq. (10) the elements of the matrices $L_{gs}^{\sigma}(t)$ and $\mathbf{L}_{n}^{-\sigma}(t)$ can also be found explicitly (see Ref. 23). In zeroth approximation we now write, instead of Eqs. (14) and (27),

$$\frac{d}{dt}|f^{\sigma}(t)\rangle_0 = -\{\mathbf{L}_0{}^{\sigma} + \Gamma_0\delta_{lk}\}|f^{\sigma}(t)\rangle_0 \tag{28a}$$

$$\frac{d}{dt}n_0(t) = -\Gamma_0 n_0(t) + C \tag{28b}$$

where

$$\mathbf{L}_0{}^{\sigma} = \mathbf{L}_{gs}^{\sigma}(\infty) - \delta_{l1}\delta_{1k}\Gamma_0, \qquad \Gamma_0 = \Gamma^{-}(0)\{n(0)/[n(\infty) - n(0)]\} \tag{28c}$$

The constant C in Eq. (28b) is determined such that the following boundary conditions are satisfied:

$$n_0(0) = n(0), \qquad n_0(\infty) = n(\infty), \qquad \left.\frac{dn_0}{dt}\right|_{t=0} = \Gamma^{-}(0)n(0), \qquad \left.\frac{dn_0}{dt}\right|_{t=\infty} = 0 \tag{29}$$

Then Eq. (28a) satisfies the boundary conditions $|f^{\sigma}(0)\rangle_0 = |f^{\sigma}(0)\rangle$ and $|f^{\sigma}(\infty)\rangle_0 = |f^{\sigma}(\infty)\rangle$. The matrix $\mathbf{L}_{gs}^{\sigma}$ can be diagonalized (see the appendix),

$$\mathbf{L}_0{}^{\sigma}|\Psi'^{\sigma}(x)\rangle = \Lambda^{\sigma}(x)|\Psi'^{\sigma}(x)\rangle, \qquad \mathbf{L}_0{}^{\sigma}|\Psi'_0{}^{\sigma}\rangle = \Lambda_0{}^{\sigma}|\Psi'_0{}^{\sigma}\rangle \tag{30a}$$

with the lowest eigenvalue $\Lambda_0{}^{\sigma} = 0$ and the spectrum

$$\Lambda^{\sigma}(x) = \Gamma_0 + 2W_0{}^{\sigma}(1 + q_{\sigma} - 2\sqrt{q_{\sigma}}\cos x) = \Gamma_0 + \lambda^{\sigma}(x) \tag{30b}$$

The coordinates $\Psi'_l{}^{\sigma}(x) = \langle l|\Psi'^{\sigma}(x)\rangle$ of the right eigenvectors are

$$\begin{aligned} \Psi'^{\sigma}_{l0} &= [q_0^{l-1}f_l{}^{\sigma}(\infty)]^{1/2} \\ \Psi'_l{}^{\sigma}(x) &= 2[q_{\sigma}^{l-1}W_0{}^{\sigma}/\lambda^{\sigma}(x)]^{1/2}[(\sqrt{q_{\sigma}} - \cos x)\sin lx + \sin x\cos lx] \end{aligned} \tag{31}$$

while the coordinates $\langle\Psi'^{\sigma}|l\rangle = \overline{\Phi}_l{}^{\sigma}$ of the left eigenvectors $\langle\Psi'^{\sigma}|$ are

$$\begin{aligned} \overline{\Psi'}^{\sigma}_{l0} &= [q_{\sigma}^{-(l-1)}f_l{}^{\sigma}(\infty)]^{1/2} \\ \overline{\Psi'}_l{}^{\sigma}(x) &= 2[q_{\sigma}^{-(l-1)}W_0{}^{\sigma}/\lambda^{\sigma}(x)]^{1/2}[(\sqrt{q_{\sigma}} - \cos x)\sin lx + \sin x\cos lx] \end{aligned} \tag{32}$$

These eigenvectors are orthonormal

$$\langle\Psi'^{\sigma}(x)|\Psi'^{\sigma}(x')\rangle = \delta(x - x'), \qquad \langle\Psi'_0{}^{\sigma}|\Psi'^{\sigma}(x)\rangle = 0, \qquad \langle\Psi'_0{}^{\sigma}|\Psi'_0{}^{\sigma}\rangle = 1 \tag{33}$$

and satisfy a closure relation

$$|\Psi_0{}^\sigma\rangle\langle\Psi_0{}^\sigma| + (1/\pi)\int_0^\pi dx\,|\Psi^\sigma(x)\rangle\langle\Psi^\sigma(x)| = 1 \tag{34}$$

Hence the solution of Eq. (28a) is found as

$$\begin{aligned} |f^\sigma(t)\rangle_0 = {} & |\Psi_0{}^\sigma\rangle\langle\Psi_0{}^\sigma|f^\sigma(0)\rangle + (1/\pi)\int_0^\pi dx \\ & \times \{\exp[-\Lambda^\sigma(x)t]\}|\Psi^\sigma(x)\rangle\langle\Psi^\sigma(x)|f^\sigma(0)\rangle \end{aligned} \tag{35}$$

where the first (time-independent) term on the right-hand side represents $|f^\sigma(\infty)\rangle$: This zero eigenvalue $\Lambda_0{}^\sigma = 0$ is a consequence of the detailed balance condition, $(L_0{}^\sigma + \Gamma_0)|f^\sigma(\infty)\rangle = 0$.

From Eqs. (16) and (17) we then find in linear response in this approximation

$$\begin{aligned} \Phi_{\mu\mu}^{(0)}(t) &= 2\lim_{\Delta H\to 0}\frac{\langle l|n^-(\infty)\rangle - \langle l|n^-(t)\rangle}{\langle\mu(0)\rangle - \langle\mu(\infty)\rangle} \\ &= 2\lim_{\Delta H\to 0}\frac{\langle l|f^-(\infty)\rangle n(\infty) - \langle l|f^-(t)\rangle n(t)}{\langle\mu(0)\rangle - \langle\mu(\infty)\rangle} \end{aligned} \tag{36}$$

which gives

$$\begin{aligned} \Phi_{\mu\mu}^{(0)}(t) = {} & -2\lim_{\Delta H\to 0}\frac{1}{\langle\mu(0)\rangle - \langle\mu(\infty)\rangle}\left(\frac{n(0) - n(\infty)}{1 - q_-}\exp(-\Gamma_0 t)\right. \\ & + n(\infty)\frac{1}{\pi}\int_0^\pi dx\,\{\exp[-\Lambda^-(x)t]\} \\ & \left. \times \langle l|\Psi^-(x)\rangle\langle\Psi^-(x)|f^-(0)\rangle\right) \end{aligned} \tag{37}$$

One then finds (for details of the algebra see Ref. 23)

$$\langle l|\Psi^-(x)\rangle = -4[W_0{}^-/\lambda^-(x)]^{3/2}\sqrt{q}_-\sin x \tag{38a}$$

$$\begin{aligned} \lim_{\Delta H\to 0}\langle\Psi^-(x)/f^-(0)\rangle = {} & 4[W_0{}^-/\lambda^-(x)]^{3/2} \\ & \times [(1 - q_-)/\sqrt{q}_-]\sin x \lim_{\Delta H\to 0}[q_- - q_-(0)] \end{aligned} \tag{38b}$$

where q_σ refers to the final thermal equilibrium (at $t = \infty$). One then finds

$$\Phi_{\mu\mu}^{(0)}(t) = e^{-\Gamma_0 t}\left\{\frac{q_+ - q_-}{(1 - q_-)(q_+ + q_-)} + q_- \frac{(2 - q_+ - q_-)(1 - q_-)^2}{q_+ + q_-}\right. \\ \times \frac{2}{\pi}\int_0^\pi \frac{dx \sin^2 x}{(1 - q_- - 2\sqrt{q_-}\cos x)^3} \\ \left. \times \exp[-2W_0^- t(1 + q_- - 2\sqrt{q_-}\cos x)]\right\} \tag{39}$$

For $t \to \infty$ the factor $e^{-\Gamma_0 t}$ with $\Gamma_0 = W_-^-(2 - q_+ - q_-)^2(1 - q_-)/(q_+ - q_-)$ dominates, while for finite t a whole spectrum of relaxation times contributes.

From Eq. (9), both $\tau_{\mu\mu}^{(0)}$ and $\tau_{\mu\mu}^{*(0)}$ can be found analytically, transforming the x-integration into contour integrals in the complex plane.(23) The result is(23)

$$\frac{1}{\tau_{\mu\mu}^{*(0)}} = \frac{(2 - q_+ - q_-)^2}{q_+ + q_-}\left\{2W_0^+ q_+ \frac{1 - q_-}{2 - q_+ - q_-} + W_-^-(1 - q_-)\frac{q_+ + q_-}{q_+ - q_-}\right\} \tag{40}$$

and

$$\tau_{\mu\mu}^{(0)} = \frac{1}{W_-^-}\frac{(q_+ - q_-)^2}{(1 - q_-)^2(2 - q_+ - q_-)^2(q_+ + q_-)} \\ + \frac{1}{2W_0^-}\frac{r_-(2 - q_+ - q_-)(1 - q_- r_-)}{(1 - q_-)(q_+ + q_-)(1 - r_-)^3} \tag{41}$$

where

$$r_\sigma = \tfrac{1}{2}(1 + q_\sigma) + \Gamma_0/4W_0^\sigma - \{[\tfrac{1}{2}(1 + q_\sigma) + \Gamma_0/4W_0^\sigma]^2 - q_\sigma\}^{1/2} \tag{42}$$

For $H/T \gg 1$ we have from Eq. (11) that $q_+ \approx 1$, $q_- \approx 0$, and then the exact equations (24) and (40) give essentially the same result. In this limit, one obtains $r_- \to 0$ and hence

$$1/\tau_{\mu\mu}^* = W_-^- + 2W_0^+, \qquad 1/\tau_{\mu\mu}^{(0)} = W_-^- \tag{43}$$

which gives in the Glauber case $\tau_{\mu\mu}^* \approx \tau_{\mu\mu}^{(0)} \approx \tau_\infty$, i.e., again a Lorentzian relaxation. Eq. (43) demonstrates that the relaxation will in general be non-Lorentzian, however.

5.2. First Approximation

In order to take into account the terms neglected in replacing Eq. (27) by Eq. (28), we introduce an evolution operator $\mathbf{U}^\sigma(t)$ by

$$|f^\sigma(t)\rangle = \exp[-(\mathbf{L}_0^\sigma + \Gamma_0\delta_{ik})t]\,\mathbf{U}^\sigma(t)|f^\sigma(0)\rangle \tag{44}$$

Writing

$$\Gamma_1(t) = \Gamma(t) - \Gamma_0, \qquad \mathbf{L}_1{}^{\sigma}(t) = \mathbf{L}^{\sigma}(t) - \mathbf{L}_0{}^{\sigma}, \qquad \mathbf{\Gamma}_1(t') = \Gamma_1(t)\delta_{lk} \tag{45}$$

we find from Eqs. (27), (44), and (45) that

$$\begin{aligned}\mathbf{U}^{\sigma}(t) = 1 - \int_0^t dt' \{\exp[(\mathbf{L}_0{}^{\sigma} + \Gamma_0\delta_{lk})t']\} \\ \times [\mathbf{L}_1{}^{\sigma}(t') + \Gamma_1(t')]\{\exp[-(\mathbf{L}_0{}^{\sigma} + \Gamma_0\delta_{lk})t']\}\mathbf{U}^{\sigma}(t)\end{aligned} \tag{46}$$

and hence

$$\begin{aligned}|f^{\sigma}(t)\rangle = |f^{\sigma}(t)\rangle_0 - \int_0^t dt' \{\exp[-(\mathbf{L}_0{}^{\sigma} + \Gamma_0\delta_{lk})(t - t')]\} \\ \times [\mathbf{L}_1{}^{\sigma}(t') + \mathbf{\Gamma}_1(t')]|f^{\sigma}(t')\rangle\end{aligned} \tag{47}$$

Our treatment is analogous to time-dependent perturbation theory in quantum mechanics. Since $\mathbf{L}_1{}^{\sigma}(t')$ and $\mathbf{\Gamma}_1(t')$ depend on the elements of $|f^{\sigma}(t')\rangle$, Eq. (47) is highly nonlinear. Nevertheless, one can introduce the usual first-order approximations, replacing the $\langle l|f^{\sigma}(t')\rangle$ by $\langle l|f^{\sigma}(t')\rangle_0$ everywhere on the right-hand side of Eq. (47). This yields

$$\begin{aligned}|f^{\sigma}(t)\rangle_1 = |f^{\sigma}(t)\rangle_0 - \int dt' \{\exp[-(\mathbf{L}_0{}^{\sigma} + \Gamma_0\delta_{lk})(t - t')]\} \\ \times [\mathbf{L}^{\sigma}_{1(0)}(t') + \Gamma_{1(0)}(t')\delta_{lk}]|f^{\sigma}(t')\rangle_0\end{aligned} \tag{48}$$

One can then show quite generally$^{(23)}$ that in this approximation the initial relaxation time τ^* is still treated rigorously. The total relaxation time $\tau^{(1)}_{\mu\mu}$ can also be obtained explicitly, although the calculation is extremely tedious.$^{(23)}$ We only quote the result$^{(23)}$:

$$\begin{aligned}\tau^{(1)}_{\mu\mu} = \frac{2 - q_+ - q_-}{q_+ + q_-}\frac{1}{(2W_0{}^-)^2}\Bigg(W_-{}^-\Bigg[(1 - q_+)^3\frac{r_+{}^2}{q_+q_-{}^2}(J^+_{32} - J^+_{22}) \\ - (1 - q_-)\frac{r_-{}^2}{q_-}J^-_{22} + \frac{(2 - q_+ - q_-)^2}{q_+ - q_-}(1 - q_-)^3\frac{r_-{}^2}{q_-}J^-_{32} \\ - (1 - q_-)^2 r_-{}^2(J^-_{21})^2\left(1 + \frac{(2 - q_+ - q_-)^2(1 - q_-)}{q_+ - q_-}\right) \\ - \frac{r_+r_-}{q_+q_-}(1 - q_+)^3(1 - q_-)J^-_{21}(J^+_{21} - J^+_{31})\Bigg] \\ + W_+{}^+\Bigg\{(1 - q_+)(1 - q_-)^2\frac{r_-{}^2}{q_-{}^3}(J^-_{22} - J^-_{32})\end{aligned}$$

$$
\begin{aligned}
&+ \frac{(1 - q_+)^2}{1 - q_-} \frac{r_+{}^2 q_+}{q_-{}^2} J_{22}^+ + (1 - q_-)^2 (1 - q_+)^2 \frac{r_+ r_- q_+}{q_-{}^3} \\
&\times J_{21}^+ (J_{31}^- - J_{21}^-) + (1 - q_-)^3 (1 - q_+) \frac{r_-{}^2}{q_-{}^3} \\
&\times \left[2\left(1 - \frac{q_-{}^2}{1 - q_-}\right) J_{32}^- - q_- (J_{21}^-)^2 \right] \Bigg\} \\
&+ 2W_0{}^- \left[r_-(1 - q_-)^2 J_{31}^- - r_- r_+ \frac{1 - q_-}{q_-} (1 - q_+)^2 J_{21}^+ J_{21}^- \right] \Bigg)
\end{aligned} \tag{49}
$$

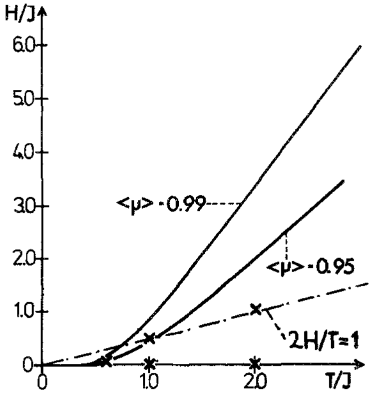
where J_{nm}^σ stands for the following integral:

$$
J_{nm}^\sigma = \frac{2}{\pi} \int^\pi dx \frac{\sin^2 x}{(1 + q_\sigma - 2\sqrt{q_\sigma} \cos x)^n [1 + (r_\sigma{}^2/\sqrt{q_\sigma}) \cos x]^m} \tag{50}
$$

These integrals can be reduced by a recursion method(23) to the integrals J_{n0} and J_{11}, which can be calculated by contour integration.(23) The integrals needed for the explicit evaluation of Eq. (49) are listed in Appendix B. We note that Eq. (49) now explicitly depends on all three rate factors $W_0{}^-$, $W_-{}^-$ and $W_+{}^+$. It has been shown(23) that $\tau_{\mu\mu}^{(1)} \rightarrow \tau_{\mu\mu}^{(0)}$ as $H/T \rightarrow \infty$, i.e., the correction terms taken into account by the "first approximation" are then negligible. This fact again justifies our whole perturbation scheme. A discussion of the numerical consequences of Eq. (49) in some cases of interest is given in Ref. 26.

Figure 7 shows the regions where $\langle\mu\rangle \geqslant 0.99$ and $\langle\mu\rangle \geqslant 0.95$ in the plane of parameter values H/J, T/J. For $2H/T > 1$ the above approximations should be reasonable. Crosses denote the parameter values where "exact" numerical solutions of Eq. (10) have been obtained (Section 4). It is clearly

Fig. 7. Temperature–field plane showing the regions of parameter values for which $\langle\mu\rangle$ exceeds 0.95 or 0.99, respectively. In the regime $2H/T \gg 1$ our first (or zeroth) approximation should be accurate. Crosses denote cases for which Eq. (10) was solved numerically.



seen that these two methods have an appreciable region of overlap. Thus, there is no need to consider higher order terms $\tau^{(n)}_{\mu\mu}$ in the perturbation expansion.

6. CONCLUSIONS

We summarize the main results of this investigation as follows:

(i) The relaxation of the generalized Glauber–Ising chain from one homogeneous state to another can be described rigorously by a set of coupled nonlinear equations [Eq. (10)] for the cluster concentrations $n_l^{\sigma}(t)$. This description holds for arbitrary values of the energy parameters H/J, T/J, and for arbitrary values of the kinetic parameters $W_0{}^+$, $W_-{}^+$, and $W_+{}^+$ of our nearest neighbor single spin-flip model. As an input, we use the rigorous results of Felderhof on the static cluster concentration in thermal equilibrium.

(ii) The initial relaxation time τ^* has been obtained exactly both in linear and nonlinear response [Eqs. (22)–(24)]. Since we show that at $T/J > 2$ a Lorentzian relaxation is appropriate for arbitrary fields, the relaxation function can be approximated by $\Phi_\mu^{\Delta e}(t) = \exp(-t/\tau^*)$. The same approximation also holds in the case of the Glauber kinetic parameters [Eq. (6)] in the regime of both T/J and H/T small. For H/T large, on the other hand, τ^* is shown to approach the single spin-flip time τ_∞ irrespective of the value of T/J. We also show that the τ^* in the linear case is usually larger than that of the nonlinear case, except for $H/T = 0$ where both cases coincide.

(iii) It is shown that the infinite hierarchy, Eq. (10), can be truncated with negligible error if $N \gg \xi^+, \xi^-$, i.e., at a truncation length much larger than the average length of clusters of up- (or down-) spins. This decoupling, hence, is well controlled, in contrast to previous work, where equations of motion for correlation functions were decoupled in a mean-field-like fashion. This truncated set has then been integrated numerically by computer for $T/J > 0.5$. We find that for $T/J < 1$ and nonzero H/T pronounced deviations from Lorentzian relaxation occur, even if one chooses the Glauber transition probabilities. For other choices of transition probabilities, some deviations occur even for $H = 0$. Thus the relaxation of the order parameter is in general polydispersive.

(iv) A perturbation treatment is presented which gives good results if the magnetization is close to its saturation value. In this regime, nucleation of (1, +)-clusters is shown to be rather unimportant. Neglecting it completely yields the "zeroth approximation," for which the Liouville operator can be explicitly diagonalized. From the resulting eigenfunction expansion, explicit expressions for the relaxation functions and the various relaxation times have been obtained. Then a time-dependent perturbation method is developed by which the neglected nucleation terms can be taken into account, and explicit expressions for the various relaxation times are derived in first order. There the initial relaxation time is already recovered exactly.

APPENDIX A. SOLUTION OF THE JACOBI EIGENVALUE PROBLEM, EQ. (30)

The matrix $\mathbf{L}_0{}^{\sigma}$ [Eq. (28c)] can be related to the well-known Jacobi oscillation matrices.(36,37) This is seen by noting that $L^{\sigma}_{gs}(\infty)$ has the structure (for N finite)

$$\mathbf{L}^{\sigma}_{gs}(\infty) = \begin{pmatrix} c_1 & -c_2 & 0 & 0 & 0 & 0 & \cdots & 0 \\ -c_1 & c & -c_2 & 0 & 0 & 0 & \cdots & 0 \\ 0 & -c_1 & c & -c_2 & 0 & 0 & \cdots & 0 \\ 0 & 0 & -c_1 & c & -c_2 & 0 & \cdots & 0 \\ \cdots & & & & & & & \\ 0 & & \cdots & 0 & -c_1 & & c & -c_2 \\ 0 & & \cdots & 0 & 0 & & -c_1 & c_2 \end{pmatrix} \tag{A1}$$

where we have introduced the abbreviations

$$c_1 = 2W_0{}^{\sigma} q_{\sigma}, \qquad c_2 = 2W_0{}^{\sigma}, \qquad c = c_1 + c_2 \tag{A2}$$

We may symmetrize $\mathbf{L}^{\sigma}_{gs}(\infty)$ or the matrix $\mathbf{J}^{\sigma} = \mathbf{L}^{\sigma}_{gs}(\infty) - \Gamma_0 \delta_{l1} \delta_{1k} + \Gamma_0 \delta_{lk}$ by an orthogonal transformation,

$$\mathbf{J}_s{}^{\sigma} = \mathbf{O} \mathbf{J}^{\sigma} \mathbf{O}^{-1}, \qquad (\mathbf{O})_{lk} = \delta_{lk} q_{\sigma}^{(l-1)/2} \tag{A3}$$

to obtain

$$\mathbf{J}_s{}^{\sigma} = \begin{pmatrix} c_1 & -(c_1c_2)^{1/2} & 0 & 0 & 0 \cdots & 0 \\ -(c_1c_2)^{1/2} & c_1 + c_2 + \Gamma_0 & -(c_1c_2)^{1/2} & 0 & 0 \cdots & 0 \\ 0 & -(c_1c_2)^{1/2} & c_1 + c_2 + \Gamma_0 & -(c_1c_2)^{1/2} & 0 \cdots & 0 \\ & & & & & \vdots \\ & & \cdot & & & 0 \\ 0 & \cdots & -(c_1c_2)^{1/2} & c_1 + c_2 + \Gamma_0 & & -(c_1c_2)^{1/2} \\ 0 & \cdots & 0 & -(c_1c_2)^{1/2} & & c_2 + \Gamma_0 \end{pmatrix} \tag{A4}$$

This matrix has rank $N - 1$, and hence one eigenvalue $\Lambda_1 = 0$ occurs. The associate eigenvector (Ψ_1) will be determined later. First we note that the eigenvalue equation $\mathbf{J}_s|\Psi_p\rangle = \Lambda_p|\Psi_p\rangle$ yields a recursion relation for the coordinates $\Psi_{l,p}$:

$$(c_1c_2)^{1/2}\Psi_{l-1,p} + (\Lambda_p - c_1 - c_2 - \Gamma_0)\Psi_{l,p} + (c_1c_2)^{1/2}\Psi_{l+1,p} = 0 \tag{A5}$$

together with two boundary conditions

$$\begin{aligned}(\Lambda_p - c_1)\Psi_{1p} + (c_1c_2)^{1/2}\Psi_{2p} &= 0\\ (\Lambda_p - c_2)\Psi_{Np} + (c_1c_2)^{1/2}\Psi_{N-1,p} &= 0\end{aligned} \tag{A6}$$

Putting $\cos\theta_p \equiv (c_1 + c_2 + \Gamma_0 - \Lambda_p)/2(c_1c_2)^{1/2}$, one finds that Eq. (A5) is solved by

$$\Psi_{l,p} = A_p \sin l\theta_p + B_p \cos l\theta_p \tag{A7}$$

where Eqs. (A6) yield two homogeneous equations for the amplitude factors A_p, B_p. Nontrivial solutions are obtained for

$$(c_1c_2)^{1/2}\Lambda_p \sin N\theta_p = 0, \qquad \text{i.e.,} \qquad \theta_p = (\pi/N)(p + n) \tag{A8}$$

where n is some integer, which we determine from the relation $\mathrm{Sp}\,\mathbf{J}_s = \sum_{l=2}^{N} \Lambda$, which gives $n = N\nu - 1$, $\nu = 0, 1, \ldots$. We choose $\nu = 0$ (other values of ν would only mean a relabeling of the eigenvalue spectrum but would not produce any physical changes), and hence we find the eigenvalues

$$\Lambda_p = c_1 + c_2 + \Gamma_0 - 2(c_1c_2)^{1/2} \cos[(\pi/N)(p - 1)] \tag{A9}$$

The coefficients A_p and B_p of the eigenfunctions $|\Psi_p\rangle$ then follow from boundary conditions (A6) together with the normalization condition $\langle\Psi_p|\Psi_{p'}\rangle = \sum_{l=1}^{N} \Psi_{lp}\Psi_{lp'} = \delta_{pp'}$:

$$A_p = \left(\frac{2c_2}{N\lambda_p}\right)^{1/2}\left[\left(\frac{c_1}{c_2}\right)^{1/2} - \cos\theta_p\right], \qquad B_p = \left(\frac{2c_2}{N\lambda_p}\right)^{1/2} \sin\theta_p \tag{A10}$$

Hence we obtain ($l = 1, \ldots, N$; $p = 2, \ldots, N$)

$$\Psi_{lp} = \left(\frac{2c_2}{N\lambda_p}\right)^{1/2}\{[(c_1/c_2)^{1/2} - \cos\theta_p] \sin l\theta_p + \sin\theta_p \cos l\theta_p\} \tag{A11}$$

The coordinates of $|\Psi_1\rangle$ follow from the closure relation $\sum_{p=1}^{N} |\Psi_p\rangle\langle\Psi_p| = 1$, or, equivalently, $\delta_{ll'} = \sum_{p=1}^{N} \Psi_{lp}\Psi_{l'p}$, to be

$$\Psi_{l1} = \{(1 - c_1/c_2)/[1 - (c_1/c_2)^N]\}^{1/2}(c_1/c_2)^{(l-1)/2}, \qquad l = 1, \ldots, N \tag{A12}$$

In the thermodynamic limit $N \to \infty$ the variable $\theta_p = (\pi/N)(p - 1)$ with $p = 2, 3, \ldots, N$ is replaced by the continuous variable x, with $0 \leqslant x \leqslant \pi$, and hence one obtains Eqs. (30) and (31).

APPENDIX B. TABLE OF INTEGRALS J_{nm} NEEDED FOR THE EVALUATION OF EQ. (49)

$$J_{21}^{\sigma} = (1 - q_{\sigma})^{-1}(1 - r_{\sigma})^{-2}$$

$$J_{22}^{\sigma} = q_{\sigma}(1 + r_{\sigma})(1 - r_{\sigma})^{-3}(1 - q_{\sigma})^{-1}(q_{\sigma} - r_{\sigma}^{2})^{-1}$$

$$J_{31}^{\sigma} = \frac{1}{2(1 - q_{\sigma})^{2}(1 - r_{\sigma})^{2}}\left(\frac{1 + q_{\sigma}}{1 - q_{\sigma}} + \frac{1 + r_{\sigma}}{1 - r_{\sigma}}\right)$$

$$J_{32}^{\sigma} = \frac{q_{\sigma}[(1 - q_{\sigma}r_{\sigma})(q_{\sigma} - r_{\sigma}^{2}) - r_{\sigma}(1 + r_{\sigma})(1 - q_{\sigma})^{2}]}{(1 - r_{\sigma})^{4}(1 - q_{\sigma})^{3}(q_{\sigma} - r_{\sigma}^{2})(q_{\sigma} - r_{\sigma})}$$

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