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Nonlinear-response theory of Ising-like systems

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The nonequilibrium response of a two-dimensional, paramagnetic system to a rapid and arbitrarily large change (quench) in a symmetry-breaking field is investigated. The complete time dependence of the conjugate order parameter is calculated with a real-space renormalization-group (RG) method. The nonlinear relaxation "rate" is found to be time dependent. Its approach to the corresponding prediction of linear-response theory is characterized. The nonlinear response is found to go over to linear response via an early, exponential regime followed by a crossover to an asymptotic, algebraic approach to linear response at long times. The initial transient decay is quench-strength dependent in contrast with the final behavior, which is largely "universal" and quench insensitive. We study a nearest-neighbor Ising model in a magnetic field in the paramagnetic, "disordered" phase. The dynamics are controlled by a kinetic Ising model with simultaneous spin-flip (adsorption-desorption) and spin-exchange (diffusion) kinetics. The model is applicable to nonequilibrium "dosing" experiments on adsorbed systems. Diffusion is shown not to affect the growth rate of the total order parameter (magnetization or coverage). General recursion relations for the temperature and magnetic field are derived for the entire thermodynamic plane. The RG analysis reproduces linear-response theory for arbitrary magnetic field and is consistent with known scaling laws concerning nonlinear relaxation. The time-dependent magnetization in the critical region has a power-law regime before crossing over into its final exponential decay.

I. INTRODUCTION

The relaxation of condensed-matter systems disturbed slightly away from equilibrium are well described by linear-response (LR) theory.[1,2] Systems subject to strong perturbations, however, do not fall within this statistical-mechanical prescription and correspondingly little is known about nonlinear relaxation. At long times, one would expect that as the system approaches equilibrium the relaxation rate coincides with that predicted by LR theory. In this paper, the nonequilibrium response of a two-dimensional, paramagneticlike system to a rapid and large change ("quench") in a symmetry-breaking field is studied. In particular, this crossover in system response from its initial nonlinear behavior to LR at long times is investigated. The response rate is initially strongly dependent on quench strength and decays exponentially in time. There is then a crossover in time to algebraic decay which is largely quench insensitive and which characterizes the asymptotic approach to the LR relaxation rate. This work is shown to have relevance to "dosing" experiments wherein adsorbed systems are suddenly exposed to adsorbate vapor.

The response of a system to an infinitesimal external influence is characterized by the fluctuation-dissipation theorem.[1,2] In this prescription, system responses to linear order in the driving force are related to equilibrium-averaged, time-dependent correlations of fluctuations in the quiescent system. No distinction is drawn between "before" and "after" as the system remains in quasiequilibrium throughout the interaction process. For finite disturbances our theoretical understanding is much less clear. A large driving force will induce a system to *evolve* to some new configuration not linearly related to the initial state.

The evolution of systems subject to sudden changes in external parameters (e.g., temperature or magnetic field) has aroused much interest in recent years.[3] Examples are nucleation and phase separation. Strongly nonequilibrium problems have been suitably investigated with numerical Monte Carlo methods.[4] However, this method has its own drawbacks, e.g., finite-size errors and problems associated with metastability. An analytic theory is desirable. From the theoretical point of view, treatment of quench problems requires the ability to handle systematically length and time scales associated with the initial and final states (and also with the intervening temporal evolution).[5] This suggests a renormalization-group (RG) approach, since RG methods were developed to handle such problems with many scales.[6] In this paper, a rather straightforward, but nontrivial, example of a strongly nonequilibrium problem is investigated using a real-space RG (RSRG) method.

We analyze this problem within the specific context of a system of particles adsorbed on a substrate subject to a sudden change in chemical potential. The model to describe the equilibrium and nonequilibrium properties of this system is discussed in Sec. II. Briefly, we employ a nearest-neighbor Ising Hamiltonian with attractive couplings to govern the equilibrium correlations with kinetics controlled by a stochastic dynamics with "spin-flip"[7] processes governing adsorption-desorption and particle-hole exchange[8] to describe diffusion. Given the well-known analogy between lattice-gas and Ising systems,[9,10] our analysis is equally well suited for describing the response of a two-dimensional spin-$\frac{1}{2}$ Ising magnet to a sudden change in external field. In the approach developed here, two space dimensions do not play a special role in the theory, and the extension to higher dimensions should be straightforward.

Aspects of this and related problems of the same universality class have been studied with field-theoretic techniques,[11,12] numerical Monte Carlo simulations,[13–16] high-temperature series-expansion methods,[17,18] mean-field theories,[19–21] and scaling-theory approaches.[21–25] Most of these works have concentrated on the nonlinear critical slowing down associated with the problem. We are interested in characterizing the complete time history of the order parameter, i.e., the surface coverage (or magnetization), from the initial moment following the quench to the final equilibrium. Critical slowing down is then a special case of our investigation. Recently,[26–28] RSRG methods have been applied to the problem of temperature quenches in Ising magnets in zero field both above and below the critical temperature. In these studies, the focus was on the nonequilibrium time dependence of the structure factor. Our work constitutes the first application of RSRG techniques to quenches in symmetry-breaking fields, and, therefore, we will restrict ourselves in this paper to the evolution of the order parameter. We will also restrict ourselves to quenches above the critical temperature. Field quenches below the critical temperature are interesting and deserve study as they can be used to investigate metastability and spinodal decomposition. This will be the object of future work.

An experimental realization of the quenching process would be the sudden injection of particles into the adsorbate gas phase initially in equilibrium with the adsorbed system such that the gas density remains constant (constant pressure) at its new value. This changes the chemical potential of the particle "source" in contact with the system of interest, and induces the adsorbates to respond by adjusting their coverage to match the new chemical potential. It is precisely this nonequilibrium evolution which is studied in this paper. During adsorption experiments, impurities are continuously "out gassing" and contaminating the system.[29] Therefore, it may be of experimental interest to know roughly how long after a "dose" one must wait before the system is effectively in equilibrium and the familiar equations of LR theory may be employed. If the system is near a second-order phase transition, as we shall see, this time may be considerable.

In LR theory, the decay of the order parameter has a simple exponential time dependence, which, within the "conventional" approximation,[30] is characterized by one decay rate.[14] This picture is expected to hold true except possibly quite near a critical point.[31–33] Precisely at the critical point, the order parameter decays algebraically in time.[11,22] In our study of the nonequilibrium order-parameter response, we generalize this relaxational time dependence by introducing so-called nonequilibrium relaxation functions.[34] In this guise, deviations from LR are easily characterized. Outside of the critical region, where "exponential" relaxation holds, we find that the "relaxation" of the order-parameter relaxation rate is time dependent and goes over to the LR decay rate in roughly two stages. To study this we introduce an analogous nonequilibrium relaxation function for the relaxation rate. For short times, the nonequilibrium decay rate relaxes toward the LR value exponentially, where *its* decay rate is strongly quench dependent. We find a crossover from exponential decay of this "metaresponse" rate to an algebraic decay which characterizes the approach to LR. The power-law exponent is found to be largely quench insensitive. In the vicinity of the critical point the order parameter relaxes at first with a nonequilibrium response, then crosses over into a power-law decay, followed by a *second* crossover into an exponential regime. This effect has been conjectured previously,[11,22] and is observed here explicitly for the first time to the best of our knowledge.

II. MODEL STUDIED

A. Equilibrium properties

Consider a set of N "spin"-$\frac{1}{2}$ variables defined on a square lattice. The basic property of these variables is their two-valued character. They can refer to adsorbed particles with no relevant internal structure (empty or occupied) or refer equally well to Ising spins (up or down). The transformation between these two pictures is well known and will not be reproduced here. (See Ref. 10 for a careful discussion.) For reasons of mathematical convenience, we work in the Ising representation. Hence, at every adsorption site, we introduce variables $\sigma_i = \pm 1$. The use of spin-$\frac{1}{2}$ language implies a hard-core repulsion, i.e., no double occupancies. The Hamiltonian governing the equilibrium properties of this system is

$$H[\sigma] = \frac{K}{2} \sum_{i,a} \sigma_i \sigma_{i+\delta_a} + BM[\sigma] , \qquad (2.1)$$

where

$$M[\sigma] = \sum_i \sigma_i \qquad (2.2)$$

is the total "magnetization." $\{\delta_a\}$ denotes the set of basis vectors connecting a given site with its four-nearest neighbors. A factor of $-\beta \equiv -(k_B T)^{-1}$ has been absorbed into the definition of the Hamiltonian. Thus K is the (dimensionless) attractive (ferromagnetic) coupling between spins, and B is a dimensionless, uniform magnetic field. In the lattice-gas picture, $4K$ is the interparticle coupling and B is a combination of K, the adsorbate-substrate binding energy, and the (uniform) adsorbate chemical potential (see Ref. 10).

The phase diagram predicted by Eq. (2.1) is well known. Briefly, there is a liquid-gas—type critical point at $u_c \equiv \tanh K_c = \sqrt{2} - 1$ and for $B = 0$ (half-coverage, $\Theta_c = \frac{1}{2}$). The associated coexistence curve is particle-hole symmetric.[35] Phase diagrams of adsorbed systems are usually more complicated than this simple picture.[10,36–38] However, many adsorbed systems[39] contain Ising-like portions in their phase diagrams.[36,40] Thus Eq. (2.1) should provide a good first approximation.

The equilibrium probability distribution is then

$$P[\sigma]=e^{H[\sigma]}\Big/\sum_{\sigma} e^{H[\sigma]} . \tag{2.3}$$

The equilibrium magnetization per site (order parameter) is

$$m=(1/N)\langle M[\sigma]\rangle , \tag{2.4}$$

where the brackets denote the usual equilibrium thermal average over $P[\sigma]$. The relationship between the order parameter in the Ising picture and that in the lattice-gas picture, the surface coverage Θ, is simply[10]

$$\Theta=\tfrac{1}{2}(1-m) . \tag{2.5}$$

This relationship extends to the nonequilibrium case as well.

B. Nonequilibrium

The time evolution of Ising models[41] is generated by a stochastic, pseudo-Liouville operator D_σ such that the time-dependent probability distribution satisfies a Markovian master equation,

$$\frac{dP[\sigma,t]}{dt}=D_\sigma P[\sigma,t] . \tag{2.6}$$

The (formal) solution of this initial-value problem is

$$P[\sigma,t]=\exp(D_\sigma t)P_I[\sigma] , \tag{2.7}$$

where $P_I[\sigma]$ is the probability distribution of the initial (prequench) equilibrium state, i.e., $P_I[\sigma]=P[\sigma,t=0]$. D_σ is constructed such that the probability distribution of the final equilibrium state is invariant under time translations. This is guaranteed by the stationarity condition,

$$D_\sigma P_F[\sigma]=0 , \tag{2.8}$$

where

$$P_F[\sigma]=\lim_{t\to\infty} P[\sigma,t] .$$

Another constraint to be satisfied by D_σ is the detailed balance symmetry.[42] We will discuss the specifics of D_σ for our model below. In the kinetic-Ising-model approach to nonequilibrium problems, all time dependence is generated by an operator characterized by the *final* equilibrium. (Thus D_σ "drives" the nonequilibrium system to this state.) This is consistent with the notion of an infinite quench rate and is also in keeping with Monte Carlo studies.[4] There have been relatively few studies with the more realistic feature of finite quench rates.[43]

Our problem of interest, then, is the computation of the nonequilibrium magnetization following a sudden change of the couplings from their initial values, $\{K_I,B_I\}$, to a new set characterizing the system in the infinite future, $\{K_F,B_F\}$,

$$m(t)=(1/N)\sum_{\sigma} M[\sigma]P[\sigma,t] . \tag{2.9}$$

In Sec. IV we describe our method for solving this problem.

The time dependence of adsorbed systems, both in and out of equilibrium, is governed simultaneously by two kinetic processes: adsorption-desorption,[44,45] whereby particles arrive at or leave the surface, and surface diffusion (hopping "migration"), the mode of transport for strongly bound particles.[46] Representing these mechanisms, we consider the total dynamical operator D_σ to be the sum of two *independent*[47] operators,

$$D_\sigma=D_\sigma^R+D_\sigma^E . \tag{2.10}$$

As independent processes, each must satisfy stationarity separately,

$$D_\sigma^R P_F[\sigma]=0 , \tag{2.11a}$$

$$D_\sigma^E P_F[\sigma]=0 . \tag{2.11b}$$

D_σ^R is a relaxational operator governing adsorption and desorption, represented by a single spin-flip operator.[48] Stochastic master equations result from coarse-graining the complete microscopic system of lattice and spins over rapidly varying degrees of freedom not germane to the study of the spin system.[41] Thus every flipped spin corresponds to a change in an adsorbate's "state." The matrix elements of D_σ^R are[49]

$$D^R[\sigma\,|\,\sigma']=\frac{-\alpha}{2}\sum_i \Lambda^{[i]}_{\sigma,\sigma'} W_i^R[\sigma']V_i[\sigma']\sigma_i\sigma_i' , \tag{2.12}$$

where $\Lambda^{[i]}_{\sigma,\sigma'}$ sets $\sigma'=\sigma$, except at site i, $W_i^R[\sigma]V_i[\sigma]$ is the spin-flip probability, and α is the microscopic rate which represents the effects of the coarse-grained degrees of freedom and sets the overall time scale. α is the flip rate in the zero-coupling (high-temperature) limit (see discussion below). Correlations among adsorbates (via "lateral" interactions) enter the transition rate through the function $W_i^R[\sigma]$, constructed to satisfy stationarity with the exact Hamiltonian, Eq. (2.1). $W_i^R[\sigma]$ is discussed in the Appendix. It should be mentioned at this point that the transition probabilities we employ in this paper are "symmetrized."[50] The Hamiltonian, Eq. (2.1), is particle-hole symmetric. It seems natural to preserve this symmetry in the dynamics. Thus $W_i^R[\sigma]$ places adsorbate and "desorbate" on equal footing, which implies that the adsorption rate is dependent upon the local environment at each site. As sticking coefficients are known to be coverage dependent,[51,52] this appears to be a reasonable supposition. It is possible to break particle-hole symmetry at the dynamical level through a suitable choice of the function $V_i[\sigma]$ above.[20,61] However, this leads to transport coefficients which do not reflect the symmetry of the underlying phase diagram.[53] In our model, we choose $V_i[\sigma]=1$.

The parameter α in the dynamical operator is identified as the basic desorption rate in the absence of lateral interactions. It is generally believed the rate of first-order desorption can be represented, at least over limited temperature ranges,[54] by an activated expression $\alpha=\alpha_0\exp(-\beta E)$ where α_0 is a frequency associated with the adsorbate-substrate interaction and E is an energy related to the heat of adsorption. This result (the Frenkel law) can be derived from simple thermodynamic and kinetic theory ideas[55] and also from transition-rate theory.[56,57] Despite recent efforts to calculate α_0 (the "preexponential" factor) microscopically,[58] experimental results show a wide discrepancy with what would be expected on theoretical grounds.[56,59] Recent experiments[59] have reported effects of lateral interactions and even phase transitions upon α_0 and other local quantities associated with desorption. Furthermore, it is thought that weakly bound precursor states can also affect the desorption rate.[60] In this paper, we ignore all such temperature and coverage effects on α and treat it as a given parameter characterizing the high-temperature state. All "slowing-down" effects on the system response will be associated strictly with adsorbate correlations which enter the operator via the transition probability and also with critical fluctuations.

Diffusion is governed by the spin-exchange operator D_σ^E, which conserves the total number of particles via a stochastic interchange of particles and holes. Kinetic Ising models have recently been applied to the study of surface diffusion.[61–66] The basic structure of D_σ^E is given by

$$D^E[\sigma\,|\,\sigma'] = \frac{-\beta}{8} \sum_{\langle ij\rangle} \Lambda_{\sigma,\sigma'}^{[i,j]} W_{ij}^E[\sigma'](\sigma_i-\sigma_j)(\sigma_i'-\sigma_j') , \tag{2.13}$$

where the sum is over exchanging pairs. $W_{ij}^E[\sigma]$ is briefly discussed in the Appendix. It is shown below that diffusion does not affect the growth of the total order parameter, and, therefore, we will not require a detailed knowledge of D_σ^E. We note here that D_σ^E leads to a particle-hole—symmetric diffusion coefficient.

β, the high-temperature hopping rate, can also be written in an activated form.[65] Since α is the pertinent time scale, we consider the ratio $R_\beta \equiv \beta/\alpha$. For a given surface, Beeby[57] has suggested a value for this ratio based on transition-rate theory. It can be shown,[67] however, that R_β is an "irrelevant" parameter in the RG sense in that it rescales to zero under iteration.

At this point, the model is completely specified. Given an initial state, $\{K_I,B_I\}$, $P_I[\sigma]$ is specified, and, given the final state, $\{K_F,B_F\}$, the dynamical operator is determined. Thus we have a well-defined, explicit means of calculating nonequilibrium averages via Eq. (2.7). First, however, we examine the structure of the theory in the limit of small quenches, i.e., LR theory.

III. LR THEORY

The response of the magnetization to a small variation in an inhomogeneous field is, to first order in the driving force,[14,68] given by the relation

$$\delta m_q(t) = \delta B_q \chi_q(t) + O((\delta B_q)^2) , \tag{3.1}$$

where $\delta m_q(t)$ is the Fourier transform of $m(t)-m_F$, and where m_F is the final magnetization, δB_q is the transform of $\delta B \equiv B_I - B_F$, and the response is given by the time-dependent susceptibility

$$\chi_q(t) = \langle \delta\sigma_{-q}\, \delta\sigma_q(t) \rangle . \tag{3.2}$$

Averages here are over the final probability distribution. $\delta\sigma_q$ is the Fourier transform of the spin fluctuation $\delta\sigma_i = \sigma_i - \langle \sigma_i \rangle$. The time development of the mode $\delta\sigma_q$ is via the "propagator"

$$\delta\sigma_q(t) = e^{\tilde{D}_\sigma t} \delta\sigma_q . \tag{3.3}$$

$\tilde{D}_\sigma$ is the adjoint operator to $D_\sigma(\tilde{D}[\sigma\,|\,\sigma'] = D[\sigma'\,|\,\sigma])$ which governs the equation of motion for observables, e.g.,

$$\frac{dM[\sigma,t]}{dt} = e^{\tilde{D}_\sigma t} \tilde{D}_\sigma M[\sigma] = e^{\tilde{D}_\sigma t} \tilde{D}_\sigma^R M[\sigma] , \tag{3.4}$$

since

$$\tilde{D}_\sigma^E M[\sigma] = 0 . \tag{3.5}$$

Equation (3.5) is the statement of the conservation law implied by the exchange dynamics.[62]

Equation (3.2) describes the time-dependent autocorrelation of fluctuations in equilibrium, the structure of which is readily seen in the memory-function representation,[2]

$$\hat{\chi}(q,z) = \chi_q[z + i\phi(q,z)]^{-1} , \tag{3.6}$$

where $\chi_q \equiv \chi_q(t=0)$ and where $\hat{\chi}(q,z)$ is the Laplace transform of $\chi_q(t)$,

$$\hat{\chi}(q,z) = -i \int_0^\infty e^{izt} \chi_q(t)\,dt . \tag{3.7}$$

The memory function $\phi(q,z)$, the generalized space- and time-dependent decay rate of equilibrium fluctuations can be shown[32] to be the sum of two pieces,

$$\phi(q,z) = \phi^{(s)}(q) + \phi^{(d)}(q,z) . \tag{3.8}$$

$\phi^{(s)}(q)$, the "static" part, is the infinite-frequency limit, and sets the initial response. It is easily shown[32] that

$$\phi^{(s)}(q) = \chi_q^{-1} \Gamma_q , \tag{3.9}$$

where the "kinetic coefficient" in our model is

$$\Gamma_q = -\langle \delta\sigma_{-q}\, \tilde{D}_\sigma\, \delta\sigma_q \rangle . \tag{3.10}$$

In the long-wavelength (hydrodynamical) limit,[69]

$$\Gamma_q = \alpha\Gamma_R + q^2\beta\Gamma_E + O(q^4) , \tag{3.11}$$

with

$$\Gamma_R = \langle W_i^R[\sigma] \rangle , \tag{3.12a}$$

$$\Gamma_E = \langle W_i^E[\sigma] \rangle . \tag{3.12b}$$

The structure of $\phi^{(d)}(q,z)$, the "dynamic" component, is rather complicated. It contains the effects of the nonlinearities in the equation of motion upon the system response.[32] It is known, for the long-wavelength and low-frequency response,[32,41] that

$$\phi^{(s)}(0) \geq \phi^{(d)}(0,0) , \tag{3.13}$$

the equality possibly occurring at the critical point. In this paper, we approximate the memory function by ignoring the dynamic part and retaining the static part, which is tantamount to the "conventional" approximation of critical dynamics.[30] In a high-temperature-series evaluation,[32] $\phi^{(d)}$ does not begin until order $(u)^4$, whereas $\phi^{(s)}$ starts at order 1. Furthermore, there is experimental[70] and Monte Carlo[64] evidence that the dynamic contribution to the system response is negligible in relation to the static contribution, except possibly in a narrow asymptotic dynamical critical region.[18,32]

Neglecting the dynamic memory function, the LR to a disturbance is then simply

$$\chi_q(t)=\chi_q e^{-\phi^{(s)}(q)t} . \tag{3.14}$$

The order parameter in our problem is the total magnetization which singles out the $q=0$ component. Thus from Eq. (3.11), the diffusive aspect of the problem does not contribute to the LR decay rate, nor is diffusion expected to play a significant role in the nonlinear relaxation. Initial correlations will decay faster via the adsorption-desorption process than they will via particle hopping. Thus diffusion would be expected to matter, if at all, only at the early stages of the magnetization relaxation. A Monte Carlo study of the one-dimensional Ising chain with simultaneous spin-flip and spin-exchange dynamics could detect no dependence upon diffusion of the magnetization relaxation within the numerical accuracy.[20]

Thus the magnetization decays within our LR theory according to the simple relationship

$$\delta m(t)=\delta m(0)e^{-\phi^{(s)}t} , \tag{3.15}$$

where $\phi^{(s)}\equiv\phi^{(s)}(q=0)$, i.e., there is *one* decay rate in the LR limit. The same result is obtained in our RG analysis, to which we now turn.

IV. RG ANALYSIS

We will solve our nonequilibrium problem via an iterative, RSRG technique. There are two main reasons for approaching the problem in this way.[26] One is that we will be concerned with the effects of the critical point upon the system response (critical slowing down). The RG is a very successful paradigm in which to study critical phenomena.[71] As we are interested in nonequilibrium dynamics, the limiting cases of the static equilibrium of the system and the dynamics of fluctuations in equilibrium must be treated in a systematic way, especially in the critical region. The RSRG is a method for handling these limits globally over the entire phase diagram, and is not restricted to the vicinity of critical points.[42] The second reason concerns the "size" of quenches. The *sine qua non* of the RG is its applicability to problems involving many scales.[6] In quench problems, one is faced with initial and final states, which if widely separated in thermodynamic properties, then one is confronted with systematically building up the time and length scales associated with the final state out of those of the initial state. Hence, in utilizing a RG approach to the study of nonequilibrium dynamics, one is not limited to near-equilibrium quenches. The aspect of competing scales becomes particularly apparent below the transition temperature where, during domain growth, large, self-similar structures are built up out of smaller ones.[27,28]

A. Equilibrium

In the RG method,[71] microscopic lengths of the system (lattice spacing) are rescaled by a factor b, which in the present instance equals 2. A Hamiltonian describing the rescaled system is obtained by coarse-graining the degrees of freedom of the original lattice which contribute to the partition function on a scale smaller than the new, effective microscopic length. There are many ways of implementing this transformation. In the coarse-graining technique employed in this paper, the renormalized Hamiltonian continues to be characterized by one coupling strength K' in a renormalized magnetic field B' in the same form as Eq. (2.1).[72,73] We will not enter into the details of the coarse-graining procedure, but instead refer to the literature where derivations can be found. We discuss below, however, the recursion relations for the renormalized coupling and field strengths, $K'=K'(K,B)$ and $B'=B'(K,B)$.

Under such a RG transformation, a general relationship between the order parameter on the original lattice and that on the rescaled lattice is given by the recursion relation

$$m(K,B)=\bar{v}(K,B)m'(K',B')+\bar{m}_0(K,B) . \tag{4.1}$$

$\bar{v}(K,B)$ and $\bar{m}_0(K,B)$ are *local* functions of the underlying degrees of freedom and, hence, represent a "clean" separation of length scales. $\bar{v}$ reflects the degrees of freedom which are projected onto the renormalized, "block" spin and $\bar{m}_0$, the remaining, short-wavelength degrees of freedom. Such a recursion relation has been derived by the authors of Ref. 74, and their notation has been adopted.[75]

Under iteration, K' and B' "flow" via *their* recursion relations to their fixed-point values (see below). This flow in coupling space in turn drives the magnetization via Eq. (4.1) to a fixed-point value, trivially evaluated exactly. In this way the magnetization of the original lattice is "built up" out of the progressively coarser scales. Thus the recursion relations for the couplings are an indispensible element in our analysis. The inclusion of a field into the RG is somewhat novel, and we must digress in this subsection to derive these recursion relations. We show below that an iterative solution of Eq. (4.1), in conjunction with our recursion relations for the couplings, compares well with the known properties of the Ising model in a magnetic field.

The "inhomogeneous" piece in the magnetization recursion relation is itself composed of other local quantities,

$$\bar{m}_0(K,B)=m_0(K,B)-\bar{v}(K,B)Q(K,B) . \tag{4.2}$$

These functions are specified in Ref. 74. The function Q plays an important role in our analysis. From Q, we obtain the renormalized magnetic field,

$$\tanh B' = Q(K,B) \; . \tag{4.3}$$

Equation (4.3) results from a locality condition imposed on the RG transformation.[74] It is shown below that this magnetic recursion relation reproduces well the exact magnetic eigenvalue associated with the flows in the critical region.

The thermal recursion relation is derived from a consideration of the exact recursion relation for the true correlation length ξ,[71]

$$\xi'(K',B') = (1/b)\xi(K,B) \; . \tag{4.4}$$

Given $B' = B'(K,B)$, Eq. (4.3), $K' = K'(K,B)$ can, in principle, be inferred.

In zero field, the "true" correlation length[76,77] is known exactly, both above and below the critical temperature.[9] From the exact $\xi(K)$, we obtain the exact thermal recursion relation (in zero field) in the "scaling field" form

$$\phi'(K') = \phi^2(K) \; , \tag{4.5}$$

where $\phi(K) = \exp(2K)\tanh(K)$. This recursion relation locates the nontrivial fixed point exactly and gives the exact thermal critical index $\nu = 1$. Thus Eq. (4.5) is a strong constraint on the more general recursion relation which includes the magnetic field.

At finite field, the correlation length is not known exactly. High- and low-temperature approximations exist;[77] however, not many terms are available in a form suitable for our analysis. Instead, we approximate Eq. (4.4) as follows. We obtain the renormalized coupling K' from a renormalization condition on static, two-point correlation functions along a line,

$$\frac{\epsilon(4R,0)}{\epsilon(2R,0)} = \frac{\epsilon'(2R,0)}{\epsilon'(R,0)} \; , \tag{4.6a}$$

where $\epsilon(i,j) = \langle \delta\sigma_i \delta\sigma_j \rangle$. This condition occurs naturally in a RG analysis of correlation functions.[42,78,79] In the limit of large R, where correlation functions decay exponentially, Eq. (4.6a) is equivalent to Eq. (4.4). However, series expansions for the correlation functions $\epsilon(i,j)$ are easily derivable for short-range correlations. Therefore, we determine K' from the *local* version of Eq. (4.6a),

$$\frac{\epsilon(4,0)}{\epsilon(2,0)} = \frac{\epsilon'(2,0)}{\epsilon'(1,0)} \; . \tag{4.6b}$$

In zero field, this condition leads to the exact thermal recursion relation in one dimension,[79] and approximately reproduces Eq. (4.5) in two dimensions.[78]

In a low-temperature, high-field, "density"-type expansion,[80] Eq. (4.6b) yields, to leading order, the recursion relation

$$[yx(1-x)]' = [yx(1-x)]^2 \; , \tag{4.7}$$

where $y = \exp(-2B)$ and $x = \exp(-4K)$ are the usual expansion variables. This equation is valid whenever x *or* y is small. This recursion relation has the same desired "scaling" form as Eq. (4.5), to which it reduces in the low-temperature, zero-field limit. At lowest order in the couplings, Eq. (4.7) yields

$$K' + B'/2 = B + 2K \; . \tag{4.8}$$

Equation (4.8) is what would be obtained from a direct analysis of Eq. (4.4) with existing low-temperature approximations of the correlation length. However, this would "miss" the more general recursion relation, Eq. (4.7).

At low temperatures, Eq. (4.3) can be shown to reduce to

$$B' = 4B[1 + O(x^2)] \; , \tag{4.9}$$

consistent with the Nienhuis and Nauenberg theorem[81] concerning low-temperature fixed points. Thus, we find the asymptotic low-temperature recursion relation

$$K' = 2K - B \; . \tag{4.10}$$

In high-temperature expansions, Eq. (4.6b) leads to the recursion relation, also in the desired form,

$$[K(1-H^2)]' = [K(1-H^2)]^2 \; , \tag{4.11}$$

for *general* field, $B(H \equiv \tanh B)$. Equation (4.11), as it stands, can also be obtained from the known approximations to ξ at high temperature. It may be verified that the high-field limit of Eq. (4.11) coincides with the high-temperature limit of Eq. (4.7). Thus the scaling-field representation of the recursion relation is seen to be valid in all the various limiting cases of the couplings K,B. Below, we assume this representation remains valid for *general* K,B over the entire thermodynamic plane.

At high temperatures, Eq. (4.3) reduces to

$$Q = H/(4-3H^2)^{1/2} \; . \tag{4.12}$$

Thus the high-temperature limit of the "pure" thermal recursion relation is

$$K' = K^2(1-H^2)(1-\tfrac{3}{4}H^2) \; . \tag{4.13}$$

A function, which, together with Eq. (4.3), interpolates between the limiting forms of the thermal recursion relation and preserves the zero-field form, is given by

$$\phi(K,B) = \exp(2K+B)\tanh[Ke^{-B}(1-H^2)] \; . \tag{4.14}$$

The obvious generalization of Eq. (4.5) is then

$$\phi'(K',B') = \phi^2(K,B) \; . \tag{4.15}$$

Supplemented with Eq. (4.3), Eq. (4.15) determines the general recursion relation for the coupling K in an arbitrary field.

Corresponding to the relevant parameters at the fixed point, we obtain the magnetic eigenvalue $y_H = 1.814$, which approximates well the exact value[71] $y_H = 1.875$, and, as mentioned above, the exact thermal eigenvalue $y_T = 1$. In Fig. 1 we present the flows defined by the recursion relations. Immediately, it is seen there are two regions in the K,B plane: one in which flows tend towards a zero-temperature, high-field fixed point, and the other in

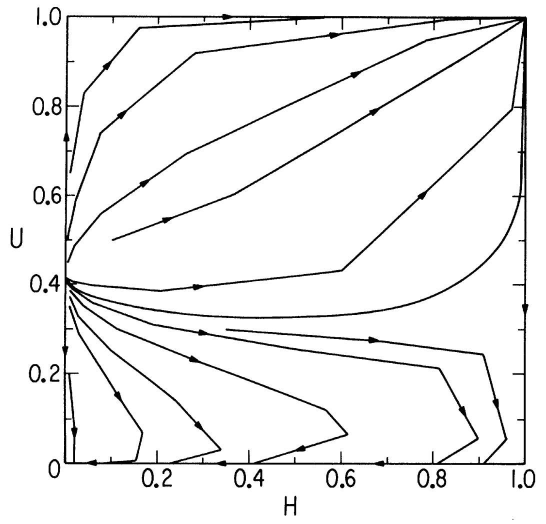

FIG. 1. "Flows" defined by recursion relations for the two couplings K,B.

which flows are attracted by a high-temperature, zero-field fixed point. There are also two other fixed points which are attracting only to the zero- and infinite-field limits, as shown. We can ascribe no physical significance to the separatrix in Fig. 1.

The magnetization obtained by iterating Eq. (4.1) is plotted in Fig. 2. Plotted is the entire field dependence for several temperatures. Also plotted is the same quantity found from series-expansion methods.[82] We plot the series results only up to $u=0.2$, as they seem unreliable for lower temperatures at large field values. (The series seem to lose "concavity.") The agreement between the two sets of curves is rather good, considering the simplicity of our assumptions.

Another static quantity of interest is the susceptibility, the recursion relation for which is found by differentiating Eq. (4.1) with respect to the field and has the same general structure as Eq. (4.1),

$$\chi=\chi_0+\bar{v}\left[\frac{\partial B'}{\partial B}\right]\chi' . \tag{4.16}$$

χ_0 is obtained via a straightforward exercise in the chain rule.

In Fig. 3 we plot the zero-field susceptibility against temperature and compare with Padé approximants both above[83] and below[76] T_c. It is seen that the amplitude is inaccurate but the critical behavior is handled correctly. We obtain the susceptibility exponent $\gamma=1.717$, within 2% of the exact $\gamma=1.75$. In Fig. 4 the critical isotherm susceptibility is plotted against the field. Again the amplitude is not well represented (too small), while the divergence is. Along the critical isotherm, the susceptibility diverges, as

$$\chi=AB^{-x} , \quad T=T_c \tag{4.17}$$

where Tarko and Fisher[76] give the amplitude $A=0.071$, and from scaling arguments, $x=\frac{14}{15}=0.933$. We obtain the exponent $x=0.946$ (within 2%) and amplitude $A=0.048$ (within 30%).

Thus we see that our simple recursion relations do a good job in calculating static quantities. They reproduce the asymptotic limits and are consistent with known properties of the Ising model. They form the foundation of our nonequilibrium analysis, which we now discuss.

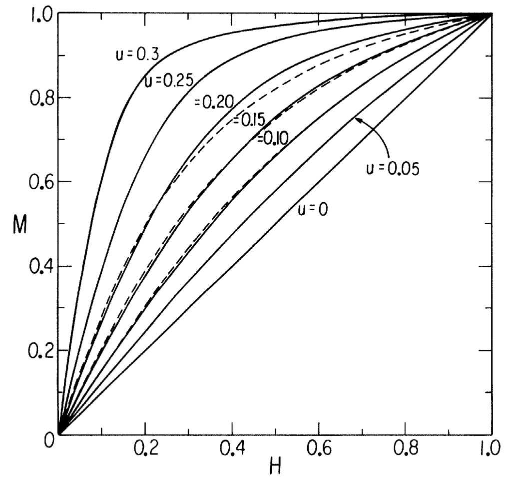

FIG. 2. Static magnetization vs magnetic field at various temperatures. Solid lines are iterated results. Dashed lines are high-temperature-series—expansion results. At high temperatures the two become indistinguishable.

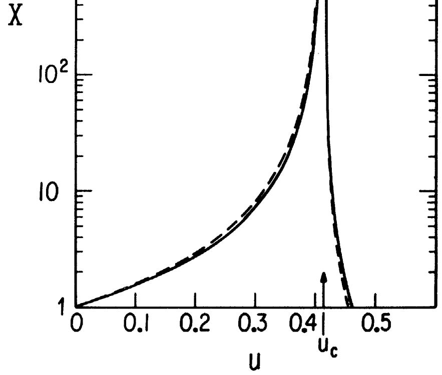

FIG. 3. Zero-field susceptibility vs temperature. Dashed lines are approximants constructed from series expansions.

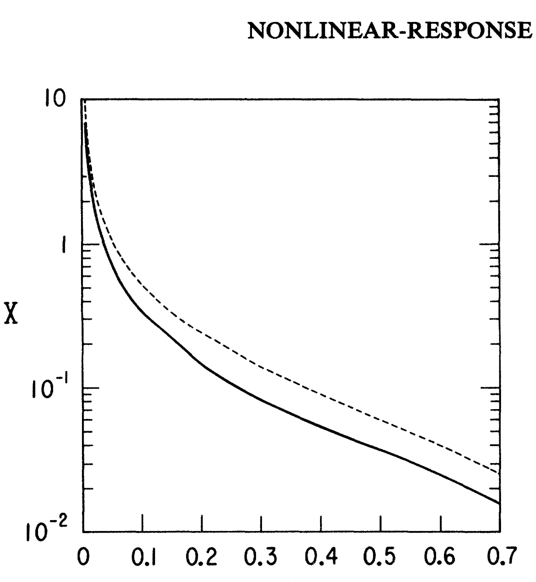

FIG. 4. Field-dependent susceptibility along critical isotherm. Dashed lines are results of Fisher and Tarko.

B. Nonequilibrium

The recursion relation for the nonequilibrium magnetization has the same structure as the corresponding quantity in equilibrium, but now generalized to include time dependence,[26,84]

$$m(t)=\bar{v}(t)m'(t')+\bar{m}_0(t) . \tag{4.18}$$

$m'(t')$ is the nonequilibrium time dependence of the coarse-grained block spin induced by a *renormalized* quench $(\{K_I',B_I'\}\to\{K_F',B_F'\})$. t' is just the time t measured in the time units associated with the rescaled lattice (see below). The function $\bar{m}_o(t)$ is the straightforward generalization of Eq. (4.2),

$$\bar{m}_0(t)=m_0(t)-\bar{v}(t)Q(t) . \tag{4.19}$$

Each of the functions in Eq. (4.19) are assumed to *relax* to equilibrium via a simple time dependence, denoted collectively by

$$x(t)=x_F+(x_I-x_F)\exp[-\Gamma^0(I,F)t] , \tag{4.20}$$

and where each decays at the same rate,[85] Γ^0. Note that the initial and final states are correctly preserved under iteration. The function Γ^0 sets the nonequilibrium response "felt" at the local level. As the system response is maximally sensitive to nonequilibrium effects in its initial stages of relaxation, Γ^0 will be determined by demanding that the short-time behavior of Eq. (4.18) match the known initial slope of the time-dependent magnetization. In the next section we discuss how the long-time properties of the relaxation are incorporated by the recursion relation.

We denote the nonequilibrium initial slope by

$$\Gamma_{\rm ne}=\left[\frac{\partial m(t)}{\partial t}\right]_{t=0} . \tag{4.21}$$

The evaluation of this quantity is discussed below. From the adjoint property of the operator and the conservation law [Eq. (3.5)], it can be shown that

$$\Gamma_{\rm ne}=\langle \tilde{D}_\sigma^R \sigma_i \rangle_I , \tag{4.22}$$

where I denotes an average over the initial probability distribution. As the operator is associated with the final state, $\Gamma_{\rm ne}$ depends on both initial and final states. It will be seen [see Eq. (4.27)] that the final state contributes to the initial slope only weakly. Equation (4.22) is another instance where diffusion does not enter the analysis.

We require the initial slope of Eq. (4.18) to reproduce Eq. (4.22). Differentiating Eq. (4.18) and inverting imposes the following condition on Γ^0:

$$\Gamma^0(I,F)=(\bar{v}_I\Delta\Gamma_{\rm ne}'-\Gamma_{\rm ne})D^{-1}(I,F) , \tag{4.23}$$

where

$$D(I,F)=m_0^I-m_0^F+(\bar{v}_I-\bar{v}_F)(m_I'-Q_I)-\bar{v}_I(Q_I-Q_F) , \tag{4.24}$$

and Δ is the time rescaling factor, $t'\equiv\Delta t$. Γ^0 is seen to be a hybrid mixture of local and global quantities. It assures us that the iterated time-dependent magnetization will have the correct initial nonequilibrium decay. Implementation of this result requires, however, an independent means of obtaining $\Gamma_{\rm ne}$.

The first step in an evaluation of $\Gamma_{\rm ne}$ is the "equation of motion" defined by $\tilde{D}_\sigma^R$,

$$\tilde{D}_\sigma^R\sigma_i=-\alpha W_i^R[\sigma]\sigma_i . \tag{4.25}$$

By substituting into Eq. (4.22),

$$\Gamma_{\rm ne}=-\alpha\langle\sigma_i W_i^R[\sigma]\rangle_I . \tag{4.26}$$

In equilibrium, this expression would vanish [Eq. (A1)], i.e., the equilibrium magnetization is constant in time. With the help of identities listed in the Appendix, we find

$$\begin{aligned}\alpha^{-1}\Gamma_{\rm ne}=&(H_F-H_I)[1+4A_I\bar{\epsilon}_I(1,0)+4A_I^2\bar{\epsilon}_I(1,1)]\\&+4(A_I-A_F)[m_I-H_F\bar{\epsilon}_I(1,0)]\\&+4(A_I^2-A_F^2)[\bar{\epsilon}_I(3)-H_F\bar{\epsilon}_I(1,1)] ,\end{aligned} \tag{4.27}$$

where the notation has been explained in the Appendix, except for

$$\bar{\epsilon}_I(3)=\langle\sigma_i\sigma_{i+\hat{x}}\sigma_{i+\hat{y}}\rangle_I . \tag{4.28}$$

We will calculate the correlation functions appearing in Eq. (4.27) with recursion-relation techniques. In other applications these could be evaluated via Monte Carlo methods. The recursion relations for $\bar{\epsilon}(1,0)$ and $\bar{\epsilon}(1,1)$ are listed in Ref. 74, and a recursion relation for $\bar{\epsilon}(3)$ may be developed with the approach discussed in the Appendix to Ref. 62. This analysis will not be reproduced here.

In Fig. 5 our results for $\Gamma_{\rm ne}$ are presented for the case of an isothermal field quench when $H_F=0$, for several temperatures, versus H_I, the initial field value. This demonstrates the "right" physics, in that the larger the quench,

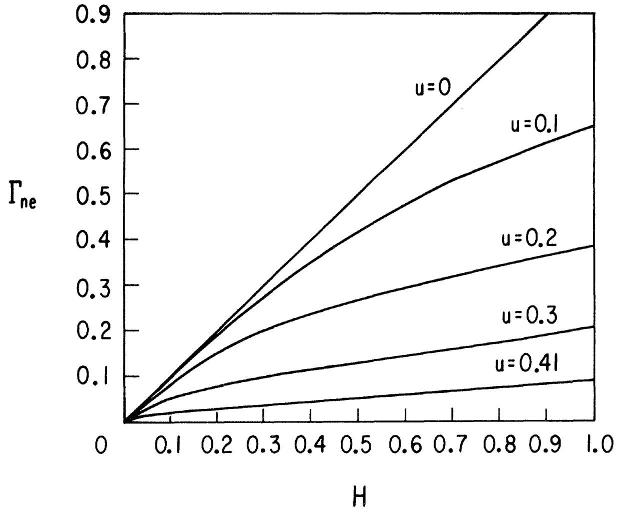

FIG. 5. Nonequilibrium initial slope corresponding to isothermal quenches at zero final field. Plotted is initial slope vs initial field value for several temperatures.

the larger the initial response. For lower temperatures, however, the initial response is less owing to the interactions among the spins. Note that Γ_{ne} remains finite at T_c.

The specification of the nonequilibrium recursion relation is not complete until the time rescaling factor Δ is determined, both because it contributes to Γ^0 [Eq. (4.23)] and because without it implementation of the recursion relation is impossible. In contrast to Γ^0, which specifies the short-time response, Δ is characteristic of the long-time aspects, and is associated with the decay rate of fluctuations in equilibrium. This requires us to examine the structure of the recursion relation in the near-equilibrium regime.

C. LR limit

The response to an infinitesimal disturbance may be examined within our RG formalism by varying Eq. (4.18) with respect to the initial state, and taking the limit of small separation between initial and final states. We will refer to the initial state approaching the final state as the LR limit. Henceforth, we shall be interested only in isothermal field quenches, which correspond most closely with what would be done in a dosing experiment. However, owing to the differences in the parameter flows between the initial and final states, the isothermal property of a quench is lost after one iteration. Thus the theory must be able to incorporate the general situation.

We define the LR function,

$$\chi(t)=\lim_{I\to F}\frac{\partial}{\partial B_I}m(t)\ . \tag{4.29}$$

From Eq. (4.18), in the LR limit, the recursion relation for this response function is

$$\chi(t)=e^{-\tilde{\Gamma}t}\chi_0+\bar{v}\left[\frac{\partial B'}{\partial B}\right]\chi'(t')\ . \tag{4.30}$$

Note that Eq. (4.30) reduces to Eq. (4.16) at zero time. $\tilde{\Gamma}$ is the LR limit of Γ^0,

$$\tilde{\Gamma}=\lim_{I\to F}\Gamma^0(I,F)\ . \tag{4.31}$$

To evaluate this limit requires a few steps. It will be seen that $\tilde{\Gamma}$ and Δ must be determined simultaneously.

First, we require the limits, both of which vanish in LR, but whose ratio does not. It can be shown that

$$\lim_{I\to F}D(I,F)=\delta B\,\chi_0\ , \tag{4.32a}$$

$$\lim_{I\to F}\Gamma_{\mathrm{ne}}=-\delta B\,\Gamma_R\alpha\ , \tag{4.32b}$$

where χ_0 appears in Eq. (4.16), and from Eq. (A7),

$$\Gamma_R=(1-H^2)\langle\tilde{W}_i[\sigma]\rangle\ . \tag{4.33}$$

Then from Eq. (4.23) we find, in the LR limit,

$$\alpha^{-1}\chi_0\tilde{\Gamma}=\Gamma_R-\bar{v}\left[\frac{\partial B'}{\partial B}\right]\Delta\Gamma_R'\ . \tag{4.34}$$

Next, to obtain the long-time structure of Eq. (4.30), we Laplace-transform [Eq. (3.7)] and obtain

$$\hat{\chi}(z)=\frac{\chi_0}{z+i\tilde{\Gamma}}+\bar{v}\frac{(\partial B'/\partial B)}{\Delta}\hat{\chi}'(z')\ , \tag{4.35}$$

where $z'=z/\Delta$ is the renormalized frequency. Inserting the memory-function representation of $\hat{\chi}(z)$, Eq. (3.6), at zero frequency, we find

$$\frac{\chi}{\phi^{(s)}}=\frac{\chi_0}{\tilde{\Gamma}}+\bar{v}\frac{(\partial B'/\partial B)}{\Delta}\frac{\chi'}{\phi'^{(s)}}\ . \tag{4.36}$$

Equations (4.34) and (4.36) form two equations in two unknowns which are readily solved to yield

$$\tilde{\Gamma}=\phi^{(s)}\ , \tag{4.37a}$$

$$\Delta=\phi^{(s)}/\phi'^{(s)}\ . \tag{4.37b}$$

These two results guarantee that the iterated solution of Eq. (4.18) will decay at long times with the LR decay rate. This holds true for arbitrary initial and final states. In the next section we show that the short-time response in the LR limit also reduces to LR theory. With Eqs. (4.37), Eq. (4.30), when iterated, yields the LR function which describes the time decay of fluctuations in equilibrium,

$$\chi(t)=\chi e^{-\phi^{(s)}t}\ , \tag{4.38}$$

in agreement with Eq. (3.14).

D. Critical limits

Before examining the iterated solutions to Eq. (4.18), we briefly consider the critical properties which can be inferred directly from scaling arguments and the recursion relations at their fixed points.

The dynamic critical index z is related to the time-rescaling factor via (the asterisk denotes fixed-point values)

$$b^{-z}\equiv\Delta^* \; . \tag{4.39}$$

From Eq. (4.37b) and scaling,

$$\Delta^*=(\chi'/\chi)^*=b^{-\gamma/\nu} \; . \tag{4.40}$$

Thus $z=\gamma/\nu$, the conventional result.[32]

The nonlinear relaxation time may be defined as[23,24]

$$\tau_{\text{ne}}=\int_0^\infty \frac{m(t)}{m(0)}dt \; . \tag{4.41}$$

As we are concerned with quenches beyond the scope of LR theory, we require an initial state such that $m(0)\gg\xi^{-\beta/\nu}$. For simplicity, we set $m(0)=1$. From Eq. (4.18),

$$\tau_{\text{ne}}=\int_0^\infty \bar{m}_0(t)dt+\frac{1}{\Delta}\int_0^\infty \bar{v}\left[\frac{t}{\Delta}\right]m'(t)dt \; . \tag{4.42}$$

The dominant contribution to the second integral comes from the final contribution to $\bar{v}(t)$. By defining τ_{ne} to diverge as $\xi^{z'}$ where $z'\neq z$,[24] from scaling and Eq. (4.42),

$$b^{z'}=(\bar{v}/\Delta)^* \; . \tag{4.43}$$

From Eq. (4.16) at the fixed point and general scaling relations,[71]

$$(\bar{v})^*=b^{-\beta/\nu} \; . \tag{4.44}$$

Thus with Eq. (4.39) we find

$$z'=z-\beta/\nu \; , \tag{4.45}$$

the Racz scaling law.[21,23] This result has recently been confirmed numerically;[16] we now verify it within a RSRG approach. z' reflects the missing "weight" under the integral from nonlinear decay (see Sec. V) induced by an initial state outside the LR regime.

Finally, if it is assumed that the magnetization at the critical point decays at long times algebraically, i.e., $m(t)\sim t^{-x}$, from Eq. (4.18) and dynamical scaling one obtains

$$b^{-zx}=(\bar{v})^* \; , \tag{4.46}$$

and thus

$$x=\beta/z\nu \; . \tag{4.47}$$

From general scaling arguments,[21–25] one expects the time-dependent equation of state, at asymptotically long times, to scale as

$$m(t)\sim\xi^{-\beta/\nu}f((t\xi^{-z})^{-x}) \; , \quad t\gg[m(0)]^{-z\nu/\beta} \; , \tag{4.48}$$

with x given by Eq. (4.47). Thus the exact $m(t)$ at the critical point decays as $t^{-1/14}$, a *very* slow decay. From our approximate recursion relation, we obtain an exponent close to this value, 1/17.7.

V. RESULTS AND DISCUSSION

A quantitative solution of the quench problem requires repeated iteration of the nonequilibrium recursion relation until the initial and final couplings have reached their respective fixed points, which define an exactly soluble, limiting quench. (See Ref. 79 for a discussion of the iteration procedure.) The iterated solution $m(t)$ depends on the five-parameter set, $\{K_I,B_I,K_F,B_F,t\}$. Clearly, many quenches may be investigated from within this set. We will concentrate on those of primary physical interest associated with dosing experiments, namely, isothermal quenches $(K_F=K_I)$ to *zero* final field. There may be, however, other cases of interest not contained within this choice. Thus we will vary independently the two parameters characterizing the initial conditions (K_I,B_I), and calculate the ensuing time dependence. Restricting B_F to zero places the final state along the line of constant critical coverage in the phase diagram, $\Theta_c=\frac{1}{2}$. This allows us to study the effects of the critical point upon the approach to equilibrium. Zero initial coverage corresponds to infinite initial field [see Eq. (2.5)].

Figure 6 is a semilogarithmic plot of the time-dependent magnetization at several temperatures. It contains much of the physics which we will subsequently examine in greater detail. The temperatures range from infinite temperature $(u=0)$ to $u=0.4$, quite close to the critical temperature $(T/T_c=1.04)$. The initial field in all cases was $H_I=0.95$, corresponding to initial coverages of 2.5% at infinite temperature and to less than 1% at $u=0.4$. Thus Fig. 6 depicts relaxations associated with *large* quenches. There are several effects with which we will be concerned here. The decay rate of the magnetization approaches the constant LR result for long times (see Sec. III). As a function of temperature, the final decay rate is seen to become smaller for lower temperatures. This is a manifestation of the interactions: It takes a progressively longer time for spins (ostensibly all in the "up" state initially) to flip when increasingly stronger lateral

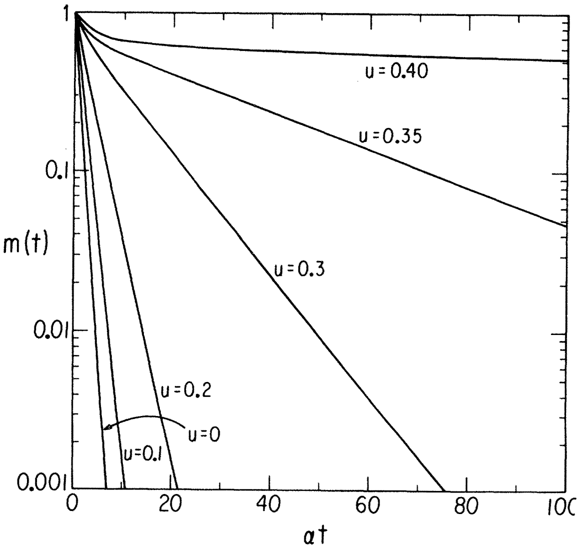

FIG. 6. Time-dependent magnetization vs time (on a semilogarithmic scale) for several temperatures following an isothermal quench. Initial field in all cases is $H_I=0.95$.

couplings tend to oppose flips and to align spins with their neighbors. As the critical temperature is approached from above, due to an increased "temperature" effect, the susceptibility begins to build up weight (see Fig. 3), and statistical considerations become important. Spin fluctuations become correlated over a large scale set by the correlation length ξ which diverges in the critical region. Overall, the final state here is one in which the order parameter is zero. However, owing to fluctuations of large extent, it takes an ever increasing amount of time for correlated "droplets" of spins to flip over. This is reflected in the basic structure of Eq. (3.9), where long-wavelength fluctuations are progressively longer lived near the critical point. Thus the dramatic slowing-down effect is seen as the temperature is lowered towards its critical value. The development of fluctuations following *temperature* quenches has been investigated recently via the time-dependent structure factor.[26] In this regard it would be interesting to monitor the structure factor following a field quench.

Of course, the initial state does not "know" what the final state will be, which brings us to another point, namely, the "curvature" at short times seen in the lower-temperature quenches in Fig. 6. This is the signature of nonlinear response. In the early stages of relaxation, the response is entirely dominated by the initial state. Suddenly, a highly correlated system has had its up-down symmetry restored and the mechanism which suppresses fluctuations removed. The initial response is controlled primarily by temperature effects associated with the initial couplings. The system eventually loses "memory" of the initially prepared state as the fluctuations characteristic of the final state have a chance to develop. It then crosses over into the final, equilibrium decay rate. We will characterize these developmental stages of the nonequilibrium response below. First, however, we digress briefly to discuss what is known about nonlinear relaxation above T_c, and how this relates to our results presented so far.

Nonequilibrium time dependence in Ising systems has received extensive investigation via Monte Carlo methods.[3,13–16] However, most of these studies have limited themselves to field and temperature quenches *below* T_c. These are complicated by the presence of the nonequilibrium aspects of first-order phase transitions.[3] We would welcome Monte Carlo comparisons in the quench regimes we have considered. One study of which we are aware focused on the pure nonlinear relaxational behavior above T_c in three and four dimensions.[16] The same curvature as in Fig. 6 was observed. As yet, there have been relatively few experimental studies designed to explicitly detect the growth of order in adsorbed systems.[86] We are aware of one experimental study of nonlinear relaxation in a non-lattice-gas system.[87] The order-parameter relaxation in a liquid-crystal system was observed to show qualitatively the same time dependence as some of the relaxations in Fig. 6.

Before further analyzing the nonequilibrium response and its crossover behavior, we examine a quench for which exact information exists. The general quench problem at infinite temperature can be solved exactly, and is a simple exponential relaxation to equilibrium,

$$m(t)=m_F+(m_I-m_F)e^{-\alpha t}\ , \quad u=0 \tag{5.1}$$

which is what would be expected of a system of noninteracting particles. Equation (5.1) is the solution to a first-order Langmuir desorption kinetics,[44,45] which characterizes many desorption systems at high temperatures, mainly those without dissociative adsorption. Note that the decay rate in this instance is *independent* of the size of the quench, a limit preserved by our RG analysis. LR theory, within the conventional approximation, is characterized by one decay rate, Eq. (3.14). Thus deviations from LR manifest themselves as "polydispersive" curved lines in a semilogarithmic plot. The LR decay rate in the high-temperature limit again is just α, independent of the field,[88] i.e.,

$$\phi(K=0,\ B)=\alpha\ . \tag{5.2}$$

Since it reproduces the nonequilibrium result exactly, the "radius of convergence" of LR theory at high temperatures is in some sense infinite, whereas in the critical region it shrinks to zero. Thus, by continuity, for moderately high temperatures and large quenches, nonlinear effects are negligible within the accuracy of Fig. 6. It will be seen, however, that for lower temperatures, nonlinear effects rapidly become evident for progressively smaller quenches. To analyze the nonequilibrium response, we now introduce a framework to discuss these effects.

Deviations from LR are conveniently investigated by introducing the relaxation function[15,34] which absorbs the initial and final states,

$$\Phi_M(t)=\frac{m(t)-m_F}{m_I-m_F}\equiv e^{-\psi(t)}\ . \tag{5.3}$$

In this way, different relaxations can be effectively compared. An exponential representation is expected to be valid over most of the thermodynamic plane, except for quenches associated with criticality, which are examined separately below. Equation (5.3) generalizes equilibrium relaxations [Eq. (3.15)] and serves to *define* the (dimensionless) function $\psi(t)$. The time dependence of ψ contains the complete history of the order-parameter relaxation. The instantaneous slope of ψ is the instantaneous rate of relaxation. Thus the approach to LR is conveniently characterized by studying the relaxation of ψ itself.

At long times, Eq. (5.3) will be proportional to the LR relaxation. Therefore, comparing Eqs. (3.15) and (5.3), the *asymptotic* structure of ψ is

$$\lim_{t\to\infty}\psi(t)=\psi_0(I,F)+\phi^{(s)}t\ , \tag{5.4}$$

where $\psi_0(I,F)$ is a (positive) proportionality constant distinguishing each quench. Hence, at long times, the *rate* of response is governed by the LR decay rate, but the order parameter itself will have further evolved during the same time period, owing to its initial nonlinear response. ψ_0

represents the cumulative effects of nonlinear response. We have no general proof that ψ_0 be positive, but stability considerations would indicate that this be the case, and every quench we have examined yields $\psi_0 \geq 0$. For quenches which drive a system into a thermodynamically unstable regime, e.g., those associated with nucleation, this condition probably breaks down. ψ_0 vanishes in the LR and high-temperature limits.

For *short* times, $\psi(t)=\dot{\psi}(0)t$ $[\psi(0)\equiv 0]$, where the dot denotes time differentiation, and where $\dot{\psi}(t)$, the instantaneous response rate, is related to the magnetization via

$$\dot{\psi}(t)=-\dot{m}(t)/[m(t)-m_F] \ . \tag{5.5}$$

The initial response rate is then [see Eq. (4.21)]

$$\dot{\psi}(0)=-\Gamma_{\rm ne}/(m_I-m_F) \ . \tag{5.6}$$

In the limit of small quenches, it can be shown that the initial response correctly reduces to LR, i.e,

$$\lim_{I\to F}\dot{\psi}(0)=\phi^{(s)} \ . \tag{5.7}$$

This amounts to the "converse" of Eq. (4.37a), where it was shown that the long-time response is given by LR for small quenches. For quenches which are small, but not vanishingly small, we have examined the approach of $\dot{\psi}(0)$ to $\phi^{(s)}$ in a high-temperature-series evaluation (the first five terms). This analysis indicates that the initial response rate is bounded from below by LR theory. While this result conforms to physical intuition, a rigorous proof is lacking. $\dot{\psi}(0)$ is bounded from above by the maximally possible quench, which corresponds to identically zero initial coverage. Thus it appears, and we find within our results, that the initial, nonequilibrium response satisfies the inequality

$$\phi^{(s)}\leq\dot{\psi}(0)\leq\Gamma_\infty \ , \tag{5.8}$$

where Γ_∞ is the maximum response rate obtained exactly from Eq. (4.27) in the infinite-field limit,

$$\Gamma_\infty=\alpha\frac{(1-u)^4}{(1+u^2)^2} \ . \tag{5.9}$$

Equation (5.8) would require modification below T_c to account for spontaneous symmetry breaking. Our RG analysis preserves the exact upper bound, Γ_∞. In Fig. 7 the two bounding functions in (5.8) are plotted against temperature. The initial response rate, then, lies between these two curves. Note the two curves merge in the infinite-temperature limit. The narrowing gap towards high temperatures explains the relative quench insensitivity seen in this regime (Fig. 6). As the critical temperature is approached, $\phi^{(s)}$ vanishes as the susceptibility diverges, and causes critical slowing down. Γ_∞, on the other hand, remains completely insensitive to critical phenomena.

In Fig. 8 the functions $\psi(t)$ obtained from a series of quenches at $u=0.3$ $(T/T_c=1.42)$ are plotted versus time (measured in units of α^{-1}). Here, we will examine the role that quench strength plays in the development of nonlinear effects. Plotted are the percentage deviations of ψ from LR, i.e., we graph $(\psi/\phi^{(s)}t-1)$ in percent against time. Thus we see that the "excess" response in comparison with LR is positive, i.e., the nonlinear response is greater than LR in conformity with Eq. (5.8). The initial fields parametrizing each quench label the curves, as shown. At this temperature, $\psi(t)$ is strongly quench dependent [see Fig. (7)]. The zero-time ordinate is related to the ratio $\dot{\psi}(0)/\phi^{(s)}$. As the quench size goes to zero, it is seen that this ratio properly approaches unity, according to Eq. (5.7). For quenches smaller than those shown, the initial response becomes rapidly diminished and the decay to LR becomes correspondingly slower. For all intents and purposes, these quenches may be said to remain

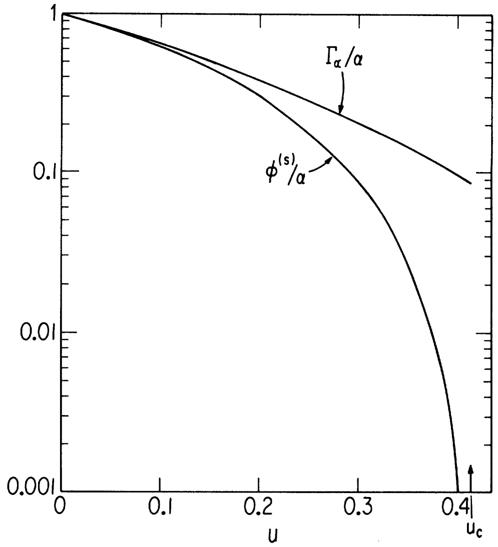

FIG. 7. Upper and lower bounds for the initial response vs temperature [see Eq. (5.8)].

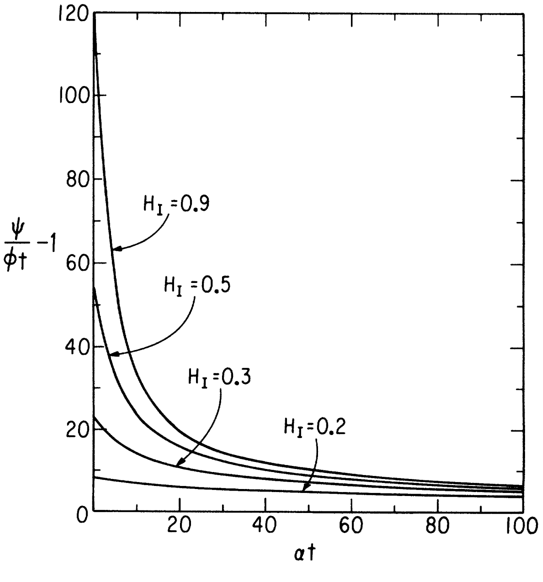

FIG. 8. Function $\psi(t)$ obtained from several quenches at $u=0.3$ vs time. Plotted is the percentage deviation from LR.

within the LR regime. This contrasts with the highly nonlinear responses associated with the larger quenches which decay *rapidly* away from the initial response rate; the stronger the quench, the more rapid this "transient" decay. The nonequilibrium relaxations are then seen to cross over into an asymptotic, *slow* approach to LR. In this asymptotic regime, the *rate* of approach towards LR is seen to be qualitatively similar among the different quenches, the only ostensible differences separating them being the constants ψ_0 [Eq. (5.4)]. We will now focus on characterizing the crossover behavior seen in Fig. 8.

The instantaneous response rate $\dot{\psi}(t)$ can also be represented with a nonequilibrium relaxation function $\widetilde{\psi}(t)$,

$$\dot{\psi}(t)=\phi^{(s)}+[\dot{\psi}(0)-\phi^{(s)}]\widetilde{\psi}(t)\ , \tag{5.10}$$

where $\widetilde{\psi}(t)$ satisfies the requirements $\widetilde{\psi}(0)=1$ and $\widetilde{\psi}(\infty)=0$. That $\dot{\psi}$ goes over to $\phi^{(s)}$ at long times is readily verified by differentiating Eq. (5.4). A natural extension of the order-parameter relaxation, it is possible to represent $\dot{\psi}$ in this manner, extracting the initial and final rates, since in both the LR and high-temperature limits $\dot{\psi}(t)$ reduces to a constant decay rate. Therefore, such a "subtraction" must be present. Equation (5.10) satisfies all limiting requirements of $\dot{\psi}$.

We find that the various stages of the relaxation of ψ seen in Fig. 8 can be effectively summarized via the following assumed form:

$$\widetilde{\psi}(t)=e^{-\omega t}+A(1-e^{-\gamma t})t^{-x}\ , \tag{5.11}$$

where $x<1$ in order to preserve the short-time constraint. Equation (5.11) is an ansatz for the purposes of discussion. $\widetilde{\psi}$ decays exponentially initially and goes over to a power-law decay at long times. However, there is no sharp break between these limiting behaviors. More properly, ω and γ should be time dependent. Clearly, we could continually regress in analyzing time-dependent rates of relaxation.

ω is the rate at which the system "forgets" its initially prepared state. This is a "nonuniversal" quantity in that it depends upon quench strength. It is observed that for the stronger the quench, the larger the rate ω. This can be understood from the following consideration. In our scheme, the larger the quench, the more ordered the initially prepared spin system. When the ordering field is suddenly turned off, the system acquires up-down symmetry for the final states we are considering. A patch of spins flipped over by a fluctuation has the same bulk energy as the reversed configuration owing to the special symmetry, the only cost in energy to create a region of the "wrong" phase coming from the surface "wall" energy, which ultimately limits the size of fluctuations. Fluctuations which were previously suppressed by the field (see Fig. 4), suddenly begin to build up to ("populate") the full regime of thermal excitations characteristic of the final state. Under this fluctuation "avalanche," the more ordered states are initially easier to destroy than the less, and thus they decay faster during this transient response regime.

We have singled out in this discussion a special final state. The results observed would seem to carry over to the more general situation, but with a diminished effect. The ratio of the final to initial susceptibilities probably sets some scale governing the size of the nonlinear response. A nonzero final field, though, destroys any critical effects.

After the period of rapid, exponential relaxation of the response rate, it crosses over and settles down to a slow evolution towards LR. This corresponds to a local equilibrium being set up as the fluctuations approach their final spectrum. The approach to LR is characterized by an algebraic decay. During this period the system has largely "forgotten" how the initial nonequilibrium state was created. There is some degree of universality in this regime, the power-law exponent being fairly insensitive to quench strength, which we find to lie approximately in the range $x=0.80$—0.85 for all quenches we have examined.

The power-law approach to LR is a fairly subtle effect. As it occurs at long times, it could easily be buried in the noise of either a Monte Carlo simulation, a real experiment, or from a contribution from $\phi^{(d)}$. Experimentally, it would mean that after a system a presumed in equilibrium, measurements fit to a form such as Eq. (3.15) would show a weakly time-dependent amplitude, which is constant in LR theory.

Finally, we examine some quenches associated with the critical point. Precisely at the critical point, the order parameter decays algebraically in time[11,22] (see Sec. IV D). However, away from the critical region, as we have seen, $m(t)$ is characterized by exponential decay. In the vicinity of the critical point, by continuity, one would expect $m(t)$ to decay with some initial nonequilibrium response and then crossover into a power-law regime, followed by a *second* crossover into the final exponential response. As one approached the critical point closer, one would expect the power-law behavior to persist for longer times before entering an exponential regime. Figure 9 is the time-dependent magnetization close to the critical temperature following a large quench ($H_I=0.95$). Labeling each curve are two numbers. One is the ratio T/T_c, the other is $u=\tanh K$. We see here explicitly the three stages of evolution described above. The initial, nonequilibrium relaxation enters a power-law "plateau," followed by a crossover into an exponential regime. For comparison, two noncritical quenches are also presented, known to decay exponentially at long times (see Fig. 6). The dashed line represents a pure power-law decay, where the slope drawn is that obtained from the critical exponents of our analysis, $x=\beta/z\nu$ [Eq. (4.47)], which we find to equal $x=1/17.7$, quite close to the exact (conventional) value $x=\frac{1}{14}$. To the best of our knowledge, this is the first time these effects have been observed explicitly. It would be interesting if these regimes could be investigated within an adsorbed system. However, this may be difficult, owing to the nearness to the critical point that is required. Efforts to obtain small reduced temperatures are hampered in adsorbed phases due to finite-size effects and imperfections.

We note that the "flatness" property of response functions, such as that in Fig. 9, is often taken as a signature of metastability.[14,15] While there is no nucleated phase

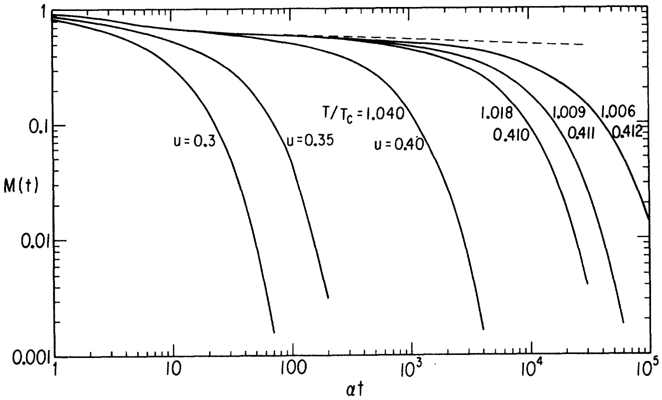

FIG. 9. Time-dependent magnetization following quenches into the critical region. Initial field value was $H_I=0.95$. Dashed line indicates the pure power-law decay at slope defined by the recursion relation.

here, the power-law behavior in Fig. 9 can be thought of as a "forerunner" to metastability.

VI. CONCLUSION

The nonequilibrium response of a two-dimensional system in its paramagnetic phase following an arbitrary quench in a symmetry-breaking field was investigated with a recursive, RG method. We have studied a fully interacting model with attractive, nearest-neighbor couplings in a magnetic field and with stochastic dynamics comprised of simultaneous spin-flip and spin-exchange kinetics. It was shown that diffusion does not affect the evolution of the total ($q=0$) order parameter. Our RG method preserves the correct initial and final states under iteration. Critical effects are handled rather well. Furthermore, the dynamics of fluctuations in equilibrium are equally well incorporated via RG analysis. The deviation of nonequilibrium response from, and the approach to, the predictions of LR theory which govern the long-time response was studied. It was found that nonlinear response approaches LR in two regimes: An initial, transient, exponential decay followed by an algebraic, asymptotic approach. The nonlinear response in the critical region was also investigated where the time-dependent magnetization was observed to have a power-law regime followed by a crossover into an exponential long-time decay.

More challenging tests of these methods would be quenches into ordered regions. Within the present model this would entail the effects of nucleation (condensation) and metastability. Extensions to more general situations would include the further-neighbor, competing interactions which give rise to the various solidlike orderings observed in adsorbed phases.[36,37] This will comprise the objects of future work.

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APPENDIX: TRANSITION PROBABILITIES

The main requirement determining the transition probability $W_i[\sigma]$ is that $W_i[\sigma]P[\sigma]$ be *independent* of site i. In this way, detailed balance and stationarity are manifestly satisfied.[42] An immediate application of this criterion is that in equilibrium,

$$\langle \sigma_i W_i[\sigma] \rangle = 0 \,. \tag{A1}$$

The nonequilibrium generalization of this result has been discussed in Sec. IV. Equation (A1) may be used to generate many useful identities.

1. Relaxational operator

Purely relaxational kinetics is a single-site process [Eq. (2.12)]. Thus,

$$W_i^R[\sigma]=\tilde{V}_i[\sigma]e^{-H^i[\sigma]} \,, \tag{A2}$$

where $H^i[\sigma]$ is any part of the Hamiltonian containing reference to site i, and $\tilde{V}_i[\sigma]$ is any spin function independent of site i. In zero field, Mazenko and Valls[42] have developed a useful form of (A2) (which implies a particular choice of $\tilde{V}_i[\sigma]$) involving only nearest- and next-nearest-neighbor correlations. This is denoted by $\tilde{W}_i[\sigma]$, where[42]

$$\tilde{W}_i[\sigma]=1+A\sigma_i\sigma_i^{\mathrm{NN}}+A^2\sigma_i^{\mathrm{NNN}} \,, \tag{A3}$$

with

$$A=-\tfrac{1}{2}\tanh(2K) \,, \tag{A4a}$$

$$\sigma_i^{\mathrm{NN}}=\sum_a \sigma_{i+\delta_a} \,, \tag{A4b}$$

$$\sigma_i^{\mathrm{NNN}}=\sum_a \sigma_{i+\delta_a}\sigma_{i+\delta_{a+1}} \,. \tag{A4c}$$

To generalize this form to include the magnetic field is trivial. We obtain, simply,

$$W_i^R[\sigma]=(1-H\sigma_i)\tilde{W}_i[\sigma] \,, \tag{A5}$$

where $H\equiv\tanh B$. Substituting (A5) into (A1), we have the identity

$$\langle \sigma_i \tilde{W}_i[\sigma] \rangle = H \langle \tilde{W}_i[\sigma] \rangle \,, \tag{A6}$$

which reduces to (A1) in zero field. Thus it is easily seen that

$$\langle W_i^R[\sigma]\rangle=(1-H^2)\langle \tilde{W}_i[\sigma]\rangle \ , \tag{A7}$$

where

$$\langle \tilde{W}_i[\sigma]\rangle=1+4A\bar{\epsilon}(1,0)+4A^2\bar{\epsilon}(1,1) \ , \tag{A8}$$

and where

$$\bar{\epsilon}(1,0)=\langle \sigma_i\sigma_{i+\hat{x}}\rangle \tag{A9a}$$

and

$$\bar{\epsilon}(1,1)=\langle \sigma_i\sigma_{i+\hat{x}+\hat{y}}\rangle \tag{A9b}$$

are the bulk correlation functions which reflect, in addition to the fluctuations, the "background" contribution of the average of each spin.

2. Diffusion

In diffusion kinetics two sites are involved. The evaluation of $W_{ij}[\sigma]$ becomes a little more complicated than for relaxational kinetics.[62] One such choice of $W_{ij}[\sigma]$ in zero field, as well as others, is discussed in Ref. 62. Since nowhere in this paper is $W_{ij}[\sigma]$ needed explicitly, we do not write it. We note only that to preserve Eq. (A1), it is necessary to include the magnetic fields in the transition probability, i.e.,

$$W_{ij}^E[\sigma]=(1-H\sigma_i)(1-H\sigma_j)W_{ij}[\sigma,H=0] \ . \tag{A10}$$

It is tempting to "eliminate" these factors through the "kinematical" spin-exchange terms in Eq. (2.13).

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