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Linear and Nonlinear Relaxation and Cluster Dynamics Near Critical Points

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The critical slowing down of anisotropic magnets, binary mixtures, and systems undergoing structural transitions is interpreted in terms of suitable defined "clusters," their growth, and their motions (cluster reactions, cluster diffusion, and cluster waves). Our previous studies of the Glauber model are extended considerably by numerical calculations, including the use of the cluster model of Reatto and Rastelli. The behavior of the relaxation function is very insensitive to the details of the models used. A scaling theory of nonlinear response is given, which is far more general than the cluster dynamics treatment. Two different cases occur: (i) at fixed "relative nonlinearity" the critical exponents agree with the corresponding exponents of linear response; (ii) if the initial state is held fixed, different exponents are found, however, which agree with predictions of Racz, and are consistent with Monte Carlo simulations of the nonlinear slowing down of the energy in kinetic Ising models.

KEY WORDS: Critical points; relaxation; clusters; cluster waves; linear response; nonlinear response; Ising models; Glauber models; lattice dynamics.

1. INTRODUCTION

Since the pioneering work of Ogita *et al.*,(1) where a model study of the order–disorder transition in ferroelectric KDP was attempted by computer simulation of an Ising system, it has been well known that critical fluctuations may, at least in principle, be interpreted in terms of "clusters" and their dynamics. Qualitative ideas along these lines have been expressed for anisotropic magnets,(2,3) ferroelectrics,(4) structural phase transitions,(5–9) and critical binary mixtures.(10) As far as quantitative predictions are concerned, this approach suffered severely from the lack of a precise formulation, and hence the "cluster dynamics" has largely been made responsible for hitherto less

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well-understood phenomena$^{(4,9)}$ (e.g., the "central peak" at structural phase transitions, etc.; see, e.g., Ref. 11 for a review).

In order to judge the validity of such conjectures, and to provide other useful information, since it would mean the explicit calculation of the dynamic response function $\chi(q, \omega)$, clearly a more systematic approach is necessary, where the dynamic evolution of the "microstates" of the system is reformulated in terms of the cluster pattern.[2] In previous work$^{(12-14)}$ we developed such an approach, which was restricted to highly anisotropic magnets$^{(12,13)}$ and binary mixtures,$^{(14)}$ however. Furthermore, while the method$^{(12,13)}$ was rather general, explicit examples have been given in very few cases only, where the Fisher cluster model$^{(15)}$ was used for the static properties of clusters. While this model is a fairly good description of clusters in the two-dimensional Ising model below T_c,$^{(16)}$ it is quite uncertain to what extent it has a more general validity.$^{(17,18)}$ Hence an extension of the approach of Refs. 12–14 is desirable in two respects: (i) derivation of explicit results in more general cases, including the use of cluster models other than that of Fisher$^{(15)}$; (ii) extension of the method to other systems, such as liquid–gas systems near their critical point, structural phase transitions, etc. The present paper gives such extensions, concentrating upon (i), and sketching only the nature of the general approach for (ii) rather than presenting complete explicit results for the dynamic response functions. To obtain the latter, further extensive calculations are required. Nevertheless, it is hoped that our treatment will contribute to elucidate the validity of other tentative approaches.$^{(4-10)}$

The outline of the paper is as follows. In Section 2 the physical meaning of "clusters" and the appropriate choice of cluster coordinates and cluster models are briefly discussed. Starting from model Hamiltonians for the considered systems in Section 3, kinetic equations for the cluster concentrations are written down, and the dynamic susceptibilities are expressed formally in terms of cluster response functions. The behavior of these cluster response functions is discussed qualitatively. Section 4 then contains various explicit quantitative calculations of these response functions for the case of the Glauber model. In Section 5 a theory of nonlinear slowing down is given, which is *not* restricted to the cluster approach. Section 6 contains our conclusions.

2. PHYSICAL MEANING AND PROPERTIES OF "CLUSTERS"

If the state of the considered d-dimensional system ($d \geqslant 2$) is described by some order parameter field $\mu(\mathbf{r}, t)$ normalized such that $\langle\mu(\mathbf{r}, t)\rangle_{T=0} = 1$, the behavior near T_c will be characterized by $\langle\mu(\mathbf{r}, t)\rangle_{T\to T_c} \ll 1$, but $\langle\mu(\mathbf{r}_1, t)\mu(\mathbf{r}_1 + \mathbf{r}, t)\rangle \gg \langle\mu(\mathbf{r}_1, t)\rangle^2$ for distances r smaller than the cor-

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[2] Some attempts in this direction also have been undertaken in Refs. 8 and 10. The drawbacks of these approaches will be discussed in more detail in Section 3.

relation length ξ. It is natural to associate clusters with the fluctuations of the local order parameter that give rise to these correlations, and hence it is clear that close to T_c large clusters must become important. The larger a cluster, the slower its relaxation, and therefore the features of the critical slowing down are reflected in the cluster dynamics. There is considerable uncertainty about what is meant precisely by a cluster, however,(13) and clearly no unique, unambiguous cluster definition is possible. Different prescriptions of what is meant by a cluster will result in different cluster properties. Since the clusters are only an intermediate step in our semiphenomenological description of the system, these prescriptions must be equivalent to each other to the extent that this ambiguity does not show up in the final results on the dynamic susceptibilities. Hence our strategy will be to choose a cluster definition such that the resulting description in terms of the clusters is as simple as possible.

As an illustration of these remarks, we consider the Ising model where $\mu(\mathbf{r}, t) = \mu_i\, \delta(\mathbf{r} - \mathbf{r}_i)$, with $\mu_i = \pm 1$ on all lattice sites $\mathbf{r}_i$. Considering a ferromagnetic state with $\langle \mu_i \rangle > 0$, it is convenient for some purposes(17) to consider groups of N reversed spins as a cluster,[3] if each of these spins is linked to at least one other spin of the cluster by a nearest neighbor bond.[4] It turns out, however, that in this case, even at infinite temperature, large clusters are important for values of the normalized field $\mu_B H/k_B T > 0$ chosen such that $\langle \mu_i \rangle$ is close to the percolation threshold.(19) For fields not exceeding this threshold even an infinite cluster occurs, i.e., in the thermodynamic limit a finite fraction of the reversed spins belongs to one interpenetrating network.[5] Since these phenomena, which occur even at infinite temperature, are obviously not related to the phase transition at $T = T_c$, the above cluster definition is clearly not a convenient one.(13) We want a definition by which no infinite clusters occur, but rather that clusters occur frequently in the system up to size ξ, while the concentration of clusters with linear dimensions much larger than ξ should be very small(2): Then the clusters represent the critical fluctuations of the order parameter in the system in a natural way.

Similar to the scaling(20) and renormalization group(21) approaches, we may make these ideas more quantitative by introducing a coarse-grained order parameter $\psi(\mathbf{r}, t)$,

$$\psi(\mathbf{r}, t) = (1/V) \sum_{i \in V} \mu_i(t) \tag{1}$$

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[3] Note that in Ref. 17, N is denoted by l and l by l'.

[4] This definition is equivalent to the prescription in which a cluster is defined via the "contour" which is drawn around the reversed spins. See Ref. 17 for a more detailed discussion, including references to earlier work.

[5] In three-dimensional Ising lattices with nearest neighbor interactions this effect happens in zero field even for a range of temperatures below T_c; see Ref. 18.

where the coarse-graining is done over cells of some volume V. This volume V is centered at $\mathbf{r}$ and satisfies the inequality $a^3 \ll V \ll \xi^3$, where a is the lattice spacing. By this procedure the variable $\mu_i(t)$, which varies rapidly from one lattice site to the next, is replaced by a function which varies smoothly as a function of $\mathbf{r}$ *for "typical" spin configurations* in the critical region, and degrees of freedom irrelevant$^{(21)}$ for the critical behavior are thus eliminated. In the usual approaches$^{(21,22)}$ one then postulates a free-energy functional $F[\psi(\mathbf{r})]$ by

$$\exp\{-F[\psi(\mathbf{r})]/k_BT\} = \operatorname*{Tr}_{\{\mu_i, i\in V\}} \exp\{-\mathscr{H}[\mu_i]/k_BT\} \tag{2}$$

where $\mathscr{H}$ is the Hamiltonian of the system. While mean-field treatments take into account only the "average configuration" $\bar{\psi}$ which minimizes F, one would have to include the effect of fluctuations by a renormalization group approach, for instance. Here instead we try to account for order parameter fluctuations by decomposing $\psi(\mathbf{r})$ into a background term $\langle\psi\rangle_b$, which has to be determined self-consistently, and a set of "clusters"$^{(13)}$ (shaded regions in Fig. 1). We say that a cluster labeled by coordinate l and center of gravity $\mathbf{r}$ occurs if there exists a connected region of space $V_l > V$ in which the excess order parameter $\psi - \langle\psi\rangle_b$ does not change sign (if it is positive, we label the cluster by $+$, and if negative, by $-$). The coordinates l and $\mathbf{r}$ are determined as

$$\begin{aligned} l &= \left| \int_{V_l} d\mathbf{r}'[\psi(\mathbf{r}') - \langle\psi\rangle_b] \right| \\ \mathbf{r} &= l^{-1} \left| \int_{V_l} \mathbf{r}'\, d\mathbf{r}'[\psi(\mathbf{r}') - \langle\psi\rangle_b] \right| \end{aligned} \tag{3}$$

The surface of the volume V_l occupied by this cluster must be closed but it may consist of several disconnected parts: A large l^+ cluster may contain smaller l^- clusters in its interior, and vice versa. We note that $\mathbf{r}$ in Eq. (3) may thus lie outside V_l, and that several clusters may have the same center of gravity $\mathbf{r}$. In the following we will disregard, however, any contribution of clusters whose "excess magnetization" l is smaller than some cutoff l_0 of order unity. The effect of these omitted small clusters then has to be included by a suitable adjustment of background terms (see below).

The motivation for this definition is the assumption that only rather large clusters are relevant for the critical behavior. Clearly one may avoid any difficulties with the percolation problem by suitably adjusting the constants V and l_0, and obtain clusters with not too irregular shapes, most of which will be well separated from each other and can thus be treated as effectively independent of each other. Thus it is hoped that a relatively simple description of the cluster dynamics may be obtained.

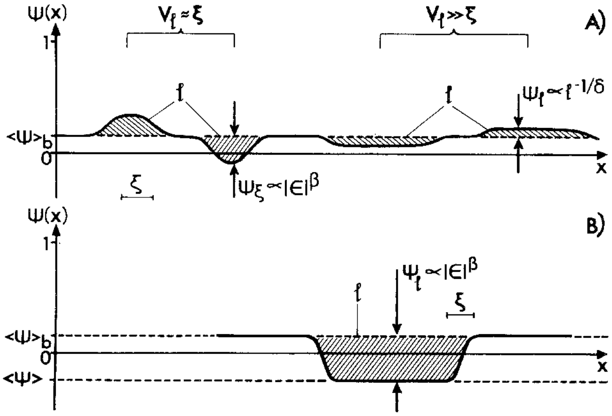

Fig. 1. Coarse-grained order parameter $\psi(x)$ plotted versus a spatial coordinate x to show various types of clusters (schematic). Case A refers to $T > T_c$, and in general nonzero field conjugate to the order parameter; case B refers to $T < T_c$ and zero field (i.e., states at the coexistence curve). The clusters of case A occur there, too, but additional domainlike fluctuations become important for large l.

If we denote the concentrations of the clusters by n_l^+ and n_l^-, the fact that by Eq. (3) a fraction c of order unity of the total volume will be filled with clusters with $l > l_0$ leads to the sum rule[6]

$$\int_{l_0}^{\infty} dl\, l(n_l^+ + n_l^-) = c \tag{4}$$

while the order parameter is given by

$$\langle\psi\rangle = \langle\psi\rangle_b + \psi_0 + \int_{l_0}^{\infty} dl\, l(n_l^+ - n_l^-) = \langle\psi\rangle_b + \psi_0 + c - 2\int_{l_0}^{\infty} dl\, l n_{l^-} \tag{5}$$

where ψ_0 is a contribution due to small clusters ($l < l_0$) not included in the integration.

Similar to the "excess magnetization" l of a cluster, we define an additional cluster coordinate E_l to measure its "excess interaction energy."

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[6] Since the scaling expressions for the $n_l^\pm$ diverge for $l \to 0$, it is convenient to introduce a cutoff l_0 with $1 \ll l_0$ but l_0 staying finite at T_c, rather than extending the integration to $l = 0$. Note that Eq. (4) can be understood as follows: Let the total number of volumes V_l in a system with total volume V_{tot} be $N^+(l)$ or $N^-(l)$, respectively. Then we may represent an integration over V_{tot} as

$$\int dl\, l[N^+(l) + N^-(l)] = \int_{V_{\text{tot}}} [\psi(\mathbf{r}) - \langle\psi\rangle_b]\, d\mathbf{r} = V_{\text{tot}} \times [\langle\psi\rangle - \langle\psi\rangle_b] = V_{\text{tot}} c$$

Since $\langle\psi\rangle_b$ is nonzero at the true T_c, one readily obtains Eq. (4), defining $n^+(l) = N^+(l)/V_{\text{tot}}$ and $n^-(l) = N^-(l)/V_{\text{tot}}$.

The total interaction energy in the system $\mathscr{H}_{\text{int}}$ is defined by $\mathscr{H} = \mathscr{H}_{\text{int}} - \mu_B H \int d\mathbf{r}\, \psi(\mathbf{r}, t)$. Then we have

$$E_l = \int_{V_l}^{\infty} d\mathbf{r}' \, \{\mathscr{H}_{\text{int}}[\psi(\mathbf{r}')] - \langle \mathscr{H}_{\text{int}} \rangle_b\} \tag{6}$$

where $\langle \mathscr{H}_{\text{int}} \rangle_b$ is the interaction energy that results from the background (i.e., the system without the clusters). Then concentrations of clusters (l, E_l) are denoted by $n^+(l, E_l)$ and $n^-(l, E_l)$, with

$$n_l^+ = \int_{E_{l0}}^{\infty} dE_l \, n^+(l, E_l), \qquad n_l^- = \int_{E_{l0}}^{\infty} dE_l n^-(l, E_l) \tag{7}$$

where E_{l0} is another cutoff with $1 \ll E_{l0}$, but E_{l0} is finite at T_c. One then obtains by arguments similar to those which gave Eq. (4) (see footnote 6) that

$$\langle \mathscr{H}_{\text{int}} \rangle = \langle \mathscr{H} \rangle_b + E_0 + \int_{l0}^{\infty} dl \int_{E_{l0}}^{\infty} dE_l \, E_l [n^+(l, E_l) + n^-(l, E_l)] \tag{8}$$

where E_0 is the contribution of the small clusters ($l < l_0$ or $E_l < E_{l0}$, respectively). In general, E_l is a variable not fixed by l, but our notation already suggests our later approximation $E_l = f(l)$.

Obviously, Eqs. (5) and (8) are valid by definition, and do not yet constitute any approximation. We now start to derive the physical properties of the cluster concentrations introduced above. Close to T_c the critical behavior shall be described by scaling expressions[7]

$$[\epsilon = (1 - T/T_c), h = \mu_B H / k_B T_c]$$

$$\langle \psi \rangle = \epsilon^{\beta} \tilde{M}(h \epsilon^{-\beta\delta}), \qquad \langle \mathscr{H}_{\text{int}} \rangle = E_c + \epsilon^{1-\alpha} \tilde{E}(h \epsilon^{-\beta\delta}), \qquad \epsilon \to 0, \quad h \to 0 \tag{9}$$

where α, β, and δ are critical exponents, E_c is the value of the interaction energy at T_c, and $\tilde{M}$ and $\tilde{E}$ are the scaling functions of magnetization and energy, respectively.(24,25) The physical reason for the singular behavior of Eq. (9) is the diverging correlation length.(24,25) Hence, obviously the contributions of the small clusters (ψ_0, E_0) cannot be responsible for the singularities of Eq. (9): Finite systems show no singularities in the partition function or its derivatives. Thus we expect n_l^- and n_l^+ to be analytic in $\epsilon = 1 - T/T_c$ at fixed l. This property has in fact been proven(26) for the somewhat analogous case of percolation clusters, where $\epsilon = 1 - p/p_c$. Therefore the singular structure of Eq. (9) must result from the integrations over large

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[7] The case of ferroelectrics is not considered in the following. There one would have to fit the cluster concentrations to the equation of state derived by Larkin and Khmelnitzkii(23) rather than to Eq. (9).

clusters up to infinite size in Eqs. (5) and (8). It can be shown(17) that this is achieved by the following homogeneity assumption(27) (see footnote 3):

$$n^-(l, E_l) \xrightarrow[h\to 0,\, \epsilon\to 0,\, l\to\infty]{} l^{-[2+(1/\delta)+(1/\beta\delta)]}\tilde{n}^-(E_l l^{-1/\beta\delta}, \epsilon l^{1/\beta\delta}, hl) \tag{10}$$

In the derivation of (10) we make use of the symmetry with respect to the change of sign $h \to -h$ and $\psi \to -\psi$, and hence

$$n^-(l, E_l, h) = n^+(l, E_l, -h) \tag{11}$$

Therefore no other homogeneity assumption for n^+ is required. Equations (10) and (8) suggest that we eliminate the integration over E_l by the following definition of energy clusters:

$$n_l^E \equiv \tfrac{1}{2} l^{-1/\beta\delta} \int_{E_{l0}}^{\infty} dE_l\, E_l[n^+(l, E_l) + n^-(l, E_l)] \tag{12}$$

such that the critical contributions of order parameter and energy can be written in the rather symmetric form (henceforth we write simply $n_l^- \equiv n_l$)

$$\begin{aligned} \langle\psi\rangle_{\text{crit}} &= -2\left(\int_{l_0}^{\infty} dl\, l n_l\right)_{\text{crit}} \\ \langle\mathscr{H}_{\text{int}}\rangle_{\text{crit}} &= 2\left(\int_{l_0}^{\infty} dl\, l^{1/\beta\delta} n_l^E\right)_{\text{crit}} \end{aligned} \tag{13}$$

where n_l and n_l^E have analogous scaling behavior(13)

$$n_l = l^{-(2+1/\delta)}\tilde{n}(\epsilon l^{1/\beta\delta}, hl), \qquad n_l^E = l^{-(2+1/\delta)}\tilde{n}^E(\epsilon l^{1/\beta\delta}, hl) \tag{14}$$

We now comment on the physical significance of these results. First it is noted that the special properties of the Ising model were *not* used at all in the derivation; hence the above results are valid for any uniaxial systems, including structural phase transitions (except ferroelectrics; see footnote 7). Second, we note that one can make a similar approach also in the "contour picture" of clusters,(17) where one works with N (number of reversed spins within a contour) and s (number of broken bonds at the surface of the exterior contour) as basic coordinates. If one avoids the percolation problem by special prescriptions,(17) one may even make a scaling assumption similar to Eq. (10). But instead of the argument hl, one then has(17) an argument hN^y, involving an additional exponent y. Eliminating this exponent by a suitable transformation of cluster coordinates $N \to l$, one may in fact switch from one cluster interpretation to the other(17) without changing the resulting equation of state. This observation illustrates a general point: Many different cluster definitions exist, e.g., "contour clusters" as usually studied in the Monte Carlo simulations,(12,13,16–18,27) "fluctuation clusters," which represent critical properties only,(2,12–15,27) and "mathematical clusters," which represent low-temperature expansion coefficients in the equation of state.(28) These various "clusters" represent different things, and will in general have different properties. For example, part of the "mathematical clusters" above T_c have negative concentration, which is impossible for physical clusters.(29) Unfortunately this distinction has been overlooked in much of the literature(15,16,18,27,28) and expressions like the Fisher cluster model,(15) which make sense in the fluctuation interpretation only, are compared to results obtained from the other definitions. Therefore much of the recent discussion(28) on clusters is inconclusive.

We conclude this section on static cluster properties by discussing more explicitly the behavior of the "fluctuation clusters" for large l. From the scaling assumption that the typical volume of the cluster should be $\sim \xi^d$, one readily finds with the help of Eq. (14) that(13,17,30)

$$V_l \propto l^{1+1/\delta}, \qquad \psi_l \equiv l/V_l \propto l^{-1/\delta} \tag{15}$$

where ψ_l is the excess order parameter density. Putting the constants of proportionality in Eq. (15) equal to unity, one finds from Eq. (15), $\xi \propto |\epsilon|^{-\nu}$, and the scaling law $d\nu = \beta(\delta + 1)$ that ψ_l for clusters with $V_l = \xi^d$ is given by $\psi_l \propto |\epsilon|^{\beta}$: For typical clusters the excess order parameter density has the same order of magnitude as the order parameter at that temperature (if $T > T_c$) or as the order parameter at the same distance $|\epsilon|$ from T_c (if $T > T_c$), in full agreement with the Ginzburg criterion for critical phenomena.

Investigating the behavior of hydrodynamic modes, i.e., modes that satisfy the condition[31] $k\xi \gg 1$, we have to study the behavior of clusters with linear dimensions $L = k^{-1}$ much larger than ξ. Then two types of fluctuations must be distinguished (Fig. 1). The first type of fluctuation is still described by Eq. (15), i.e., its excess order parameter density vanishes for $L \to \infty$ as $L^{-\beta/\nu}$. Therefore the excess energy density may be expanded as

$$\begin{aligned} &\mathscr{H}_{\text{int}}[\psi(\mathbf{r}')] - \langle \mathscr{H}_{\text{int}} \rangle_b \\ &\quad \approx \mathscr{H}_{\text{int}}[\langle \psi \rangle_b] + \left.\frac{\delta \mathscr{H}_{\text{int}}}{\delta \psi}\right|_{\langle \psi \rangle_b} [\psi(\mathbf{r}') - \langle \psi \rangle_b] - \langle \mathscr{H}_{\text{int}} \rangle_b \\ &\quad = [\psi(\mathbf{r}') - \langle \psi \rangle_b] \left.\frac{\delta \mathscr{H}_{\text{int}}}{\delta \psi}\right|_{\langle \psi \rangle_b} \end{aligned}$$

which shows that in general the typical energy $\bar{E}_l'$ of this excitation behaves as $\bar{E}_l' \propto l$. This type of fluctuation occurs throughout the whole (h,ϵ) plane. The second type of fluctuation is restricted to the vicinity of the coexistence curve below T_c, however. This fluctuation is of the domain type, i.e., its excess order parameter density is $\sim \epsilon^{\beta}$ *independent of L*. Since in the interior of this domain fluctuation the order parameter has a value corresponding to the other branch of the coexistence curve, there is no excess contribution to the interaction energy from the interior but only from the surface. Equations (10) and (12) then imply that $\bar{E}_l'' \propto |\epsilon|^{1-\alpha-\nu}L^{d-1}$.[8]

We now estimate the relative statistical weights of these two types of excitations. Since these large fluctuations require rather high formation energies $\bar{F}_l$, they occur in thermal equilibrium rather seldom and are thus noninteracting. We may estimate their concentration simply from the Boltzmann factor, $n_l \propto \exp(-\bar{F}_l/k_BT)$, and from $\bar{E}_l \propto \partial\bar{F}_l/\partial\epsilon$ we find $\bar{F}_l$ and hence

$$n_l' \propto \exp[-c_1|\epsilon|^{\beta\delta}l], \qquad n_l'' \propto \exp[-c_2|\epsilon|^{2-\alpha-\nu}L^{d-1}] \tag{16}$$

Below T_c the second type will always by far dominate for large enough L in comparison with the first. Thus we note a strong asymmetry in the properties of "fluctuation clusters" with respect to the sign of ϵ, as proposed recently also in the percolation problem.(32) Since for $L \gg \xi$ both n_l' and n_l'' are very small, the contribution of Eq. (16) to static averages is negligible, except if one considers high derivatives of the free energy with respect to either ϵ or h. An interesting consequence of n_l'' is thus the essential singularity at the coexistence curve.(15,17,33) While this singularity is hardly accessible to experimental observation, Eq. (16) may be more important for dynamic susceptibilities in the hydrodynamic regime.

Finally we mention two explicit models for the properties of clusters in the regime where V_l and ξ^d have the *same* order of magnitude: the Fisher model(15)

$$n_l = (1/a)n_l^E = q_0 l^{-(2+1/\delta)}\exp(-a\epsilon l^{1/\beta\delta} - hl) \tag{17}$$

and the model of Reatto and Rastelli(34)

$$n_l = q_0 l^{-(2+1/\delta)}[\exp(-a\epsilon l^{1/\beta\delta} - hl)/[1 + B\exp(ba\epsilon l^{1/\beta\delta})] \tag{18}$$

While Eq. (17) is restricted to $\epsilon > 0$, i.e., $T < T_c$, Eq. (18) is applicable also for $T > T_c$, where the condition $\langle\psi\rangle \equiv 0$ leads to a relation between the two parameters B and $b > 1$. The remaining parameters are fitted to critical amplitudes in the equation of state. Note that both Eq. (17) and Eq. (18) do have the correct scaling structure of Eq. (14), but neither exhibits the correct asymptotic behavior of Eq. (16). More important, Eqs. (17) and (18) are expected to be inaccurate for $|\epsilon|l^{1/\beta\delta} \ll 1$, and hence the determination of the parameter q_0, a, etc., in terms of critical amplitudes is a dubious procedure.(35) Nevertheless computer simulations(16,18) show that for $T < T_c$ and ϵ not too small and $10 \lesssim N \lesssim 100$ (there the difference between N and

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[8] We may define $\bar{E}_l = \int_{E_l^0}^{\infty} dE_l\, E_l n_l^-(l, E_l) / \int_{E_l^0}^{\infty} dE_l\, n_l^-(l, E_l)$, which gives

$$\bar{E}_l = l^{1/\beta\delta}\tilde{E}_l(\epsilon l^{1/\beta\delta}, hl),$$

showing that for typical clusters ($V_l = \xi^d$) the typical energy contribution is proportional to $l^{1/\beta\delta}$, as expected from Eq. (13). If $\tilde{E}_l(x,y)$ behaves like $|x|^{1-\alpha}$ for large x, $\bar{E}_l \propto |\epsilon|^{1-\alpha}L^d$ results.

l may be neglected), Eq. (17) gives a reasonable account of the actual cluster distribution. Therefore it is legitimate to use Eqs. (17) and (18) in order to derive explicit examples for dynamic susceptibilities. We expect that the difference between the susceptibility based on Eq. (17) and the susceptibility based on Eq. (18) below T_c will be of the same order of magnitude as the difference between either of these approximations and the true susceptibility.

3. KINETIC EQUATIONS FOR THE CLUSTER CONCENTRATIONS

3.1. Dynamic Correlations and the Cluster Response Functions

We consider the case where the system is kept for times $t < 0$ at thermal equilibrium with temperature ϵ and a field $h + \Delta h \exp(i\mathbf{xq})$. At $t = 0$, the field $\Delta h \exp(i\mathbf{qx})$ is switched off, and the system relaxes toward a new equilibrium. In particular, the cluster concentrations n_l and n_l^E will relax; we denote these time- and space-dependent concentrations by $\bar{n}_l(\mathbf{x}, t)$ and $\bar{n}_l^E(\mathbf{x}, t)$, with $\bar{n}_l(\mathbf{x}, \infty) = n_l$ and $\bar{n}_l^E(\mathbf{x}, \infty) = n_l^E$. As cluster response functions we introduce the relative deviations of the cluster concentrations from the final equilibrium by

$$g_l(\mathbf{q}, t) = \int d\mathbf{x}\,[\exp(-i\mathbf{qx})][\bar{n}_l(\mathbf{x}, t) - n_l]/n_l$$

$$g_l^E(\mathbf{q}, t) = \int d\mathbf{x}\,[\exp(-i\mathbf{qx})][\bar{n}_l^E(\mathbf{x}, t) - n_l^E]/n_l^E \tag{19}$$

Then the relaxation of the critical parts of the order parameter and energy [Eq. (13)] may be described by the following functions$^{(13)}$:

$$\phi_\mu^{\Delta H}(\mathbf{q}, t) = \int_{l_0}^{\infty} dl\, l n_l g_l(\mathbf{q}, t) \Big/ \int_{l_0}^{\infty} dl\, l n_l g_l(\mathbf{q}, 0) \tag{20a}$$

$$\phi_E^{\Delta H}(\mathbf{q}, t) = \int_{l_0}^{\infty} dl\, l^{1/\beta\delta} n_l^E g_l^E(\mathbf{q}, t) \Big/ \int_{l_0}^{\infty} dl\, l^{1/\beta\delta} n_l^E g_l^E(\mathbf{q}, 0) \tag{20b}$$

In the linear response regime, where $\Delta h = \delta h$ is infinitesimally small, Eqs. (20a) and (20b) reduce to normalized correlation functions$^{(13,36)}$

$$\phi_\mu^{\Delta H}(\mathbf{q}, t) \to \phi_{\mu\mu}(\mathbf{q}, t) = \langle \delta\psi(\mathbf{q}, t)\, \delta\psi(-\mathbf{q}, 0)\rangle / \langle \delta\psi(\mathbf{q}, 0)\, \delta\psi(-\mathbf{q}, 0)\rangle \tag{21a}$$

$$\phi_E^{\Delta H}(\mathbf{q}, t) \to \phi_{E\mu}(\mathbf{q}, t) = \langle \delta\mathscr{H}(\mathbf{q}, t)\, \delta\psi(-\mathbf{q}, 0)\rangle / \langle \delta\mathscr{H}(\mathbf{q}, 0)\, \delta\psi(-\mathbf{q}, 0)\rangle \tag{21b}$$

where $\delta\mathscr{H} = \mathscr{H} - \langle\mathscr{H}\rangle$ and $\delta\psi = \psi - \langle\psi\rangle$. If one keeps the field constant and considers a change of temperature, additional response functions $\phi_{EE}(\mathbf{q}, t)$, etc., can be defined analogously.$^{(13,36)}$ Fourier transformation of Eqs. (20)–

(21) with respect to time then yields the neutron scattering function $S(\mathbf{q}, \omega)$ usually considered in the theory of dynamic critical phenomena.(11,31)

We stress the fact that the above equations have general validity for all kinds of uniaxial systems, including ferroelectrics and structural phase transitions. Note that in the latter case the order parameter $\mu(\mathbf{r}, t)$ will be given in terms of atomic displacements $u(\mathbf{R}_j, t)$ in some preferred direction as $\mu(\mathbf{r}, t) = \sum_j [\exp(i\mathbf{Q}\mathbf{R}_j)]u(\mathbf{R}_j, t)\, \delta(\mathbf{r} - \mathbf{R}_j)$, where the sum is extended over all lattice points $\mathbf{R}_j$, and $\mathbf{Q}$ is the characteristic wave vector of the ordering. In this case $\mathbf{q}$ is a relative wave vector $\mathbf{q} = \mathbf{k} - \mathbf{Q}$, of course, and the "staggered field" h has then a formal significance only.

While the above equations are exact, approximations come in if one requires that the cluster response functions $g_l(\mathbf{q}, t)$ be determined from a "*closed*" kinetic equation rather than from a complicated hierarchy of higher order correlation functions. One expects different kinetic equations for anisotropic magnets, binary systems, and structural phase transitions, of course.

3.2. Anisotropic Magnets, Binary Systems, and the Cluster Diffusion and Reaction Equation

The static properties of both anisotropic magnets and solid binary mixtures may be described by an Ising Hamiltonian[9]

$$\mathscr{H} = -\sum_{ij} J_{ij}\mu_i\mu_j - \mu_B H \sum_i \mu_i + \lambda V + \mathscr{H}_{\text{lattice}} \tag{22}$$

In the case of the magnet, the variable μ_i represents the orientation of the spin, while in the case of the AB mixture $\mu_i = +1$ corresponds to an A atom at site i, and $\mu_i = -1$ to a B atom. The coupling term λV describes the interaction between the $\{\mu_i\}$ and the degrees of freedom of the lattice (which would be described by $\mathscr{H}_{\text{lattice}}$). In the limit where $\lambda \to 0$ the lattice and the spins are uncoupled, and static averages of the latter are those of the ordinary Ising model. In this limit the dynamics on the scale of times $t \propto \lambda^{-2}$ is described by a Markovian master equation(37) for the probability $P(\mathbf{X}, t)$, where $\mathbf{X} = \{\mu_i\}$:

$$dP(\mathbf{X}, t)/dt = -\sum_{\mathbf{X}'} P(\mathbf{X}, t) W(\mathbf{X} \to \mathbf{X}') + \sum_{\mathbf{X}'} P(\mathbf{X}', t) W(\mathbf{X}' \to \mathbf{X}) \tag{23}$$

In the magnetic case, the transitions $\mathbf{X} \to \mathbf{X}'$ will consist of single spin flips $\mu_j \to -\mu_j$ independent of each other. In the case of the alloy, stochastic

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[9] Anisotropic magnets with spin quantum number $s \neq 1/2$ have to be represented somewhat differently. This difference is insignificant, of course, when we transform to a quasicontinuous variable ψ in Eq. (1). With respect to critical exponents, dynamic scaling functions, etc., the spin quantum number is believed to be an irrelevant variable.(21)

exchange of neighboring atoms is represented by interchange of neighboring spins ($\mu_i \to \mu_j$, $\mu_j \to \mu_i$). The transition probability $W(\mathbf{X} \to \mathbf{X}')$ satisfies a detailed balance condition with the canonic distribution

$$P(\mathbf{X}) \propto \exp[-\mathscr{H}(\mathbf{X})/k_BT].$$

In the one-cluster-coordinate approximation$^{(13)}$ one obtains for $g_l(x, t)$ the following cluster diffusion and cluster reaction equation from Eq. (23)[10] (note that here $\mathbf{Q} = 0$):

$$\begin{aligned}\frac{\partial}{\partial t} g_l(\mathbf{q}, t) \\ &= R_l\left[\frac{\partial^2}{\partial l^2} g_l(\mathbf{q}, t) + \frac{\partial}{\partial l}\ln(R_l n_l)\frac{\partial}{\partial l} g_l(\mathbf{q}, t)\right] - D_l q^2 g_l(\mathbf{q}, t) \\ &\equiv L g_l(\mathbf{q}, t) - D_l q^2 g_l(\mathbf{q}, t) \end{aligned} \tag{24}$$

where R_l is the rate at which an l cluster is involved in cluster reactions, while D_l is its diffusivity.$^{(13)}$ One finds that these kinetic coefficients may be represented by power-law behavior$^{(14)}$

$$R_l \xrightarrow[l\to\infty]{} \hat{R}l^r, \qquad D_l \xrightarrow[l\to\infty]{} \hat{D}l^{-(1-1/\delta)} \tag{25}$$

where $\hat{R}$, $\hat{D}$, and r are constants. While the fact that per unit time in a volume V_l there can be no more than V_l spin flips (or exchanges, respectively) leads to an inequality $r < 1 + 1/\delta$ [cf. Eq. (15)], no arguments are known which fix the precise value of this exponent $r^{(13)}$.

For a solution of Eq. (24) the initial and boundary conditions have to be specified. From Eq. (19) we can express $g_l(\mathbf{q}, 0)$ in terms of the equilibrium cluster concentration with the field $h + \Delta h \exp(i\mathbf{x}\mathbf{q})$. The boundary condition for large l is$^{(13)}$ $\lim_{l\to\infty} n_l g_l^2(\mathbf{q}, t) = 0$. In the spin-flip model where the order parameter is not conserved we also have $\lim_{l\to 0} g_l(\mathbf{q}, t) = 0$; in the spin-exchange case the boundary condition is determined implicitly from the conservation law of the order parameter, i.e., $\int_{l_0}^{\infty} dl\, l n_l g_l(0, t) = \text{const}$. It turns out that in the latter case the asymptotic relaxation is dominated by the diffusive term in Eq. (24), i.e., Eq. (21a) behaves as $\propto \exp(-Dq^2t)$, with$^{(38)}$

$$D = \int_{l_0}^{\infty} l^2 n_l D_l\, dl \bigg/ \int_{l_0}^{\infty} l^2 n_l\, dl \tag{26}$$

With the help of Eqs. (14) and (25) one then finds $D \propto \epsilon^{\gamma}$, in agreement with other approaches.$^{(39)}$ In the recent approach of Ackerson *et al.*$^{(10)}$ the reaction terms of Eq. (24) have erroneously been omitted. This approximation leads

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[10] The equation for $g_l^E(\mathbf{x},t)$ is completely analogous, as can be shown from the symmetry relations $\Phi_{E\mu}(\mathbf{q}, t) = \phi_{\mu E}(\mathbf{q}, t)$, etc.$^{(13)}$

to a behavior of $\phi_{\mu\mu}(\mathbf{q}, t) \propto \exp(-D'q^{4/3}t^{2/3})$ at large times. This result contradicts the hydrodynamic structure $\exp(-Dq^2t)$, which is an exact consequence of the conservation law, and hence their result is a very poor approximation.

In the case without conservation laws the diffusive term in Eq. (24) gives rise only to unimportant corrections to scaling. From Eqs. (14), (24), and (25) one then readily deduces(12) that $g_l(\mathbf{q}, t)$ satisfies dynamic scaling, i.e., $g_l(\mathbf{q}, t) = l\tilde{G}(\epsilon l^{1/\beta\delta}, hl, \mathbf{q}\xi, t/\tau)$, with $\tau \propto \epsilon^{-\Delta_{\mu\mu}}$, $\Delta_{\mu\mu} = \beta\delta(2 - r)$, and the asymptotic decay of Eq. (21) for large times is a simple exponential also for $\mathbf{q} = 0$, i.e., $\phi_{\mu\mu}(0, t) \propto \exp(-t/\tau)$. More precise explicit solutions of Eq. (24) will be obtained in Section 4.

Here we are concerned with the validity of the one-cluster-coordinate approximation. While heuristic arguments in favor of this approximation have been given earlier,(13,35) here we study its extension. Defining by $g(l, E_l, t)$ the relative deviation from $n^-(l, E_l)$ similar to Eq. (19), one obtains as a generalization of Eq. (24) the result(35) (we put $\mathbf{q} = 0$ and omit the arguments l, E_l for simplicity)

$$\begin{aligned}\frac{\partial}{\partial t} g(t) = {} & R_{11}\left[\frac{\partial^2}{\partial l^2} g(t) + \frac{\partial}{\partial l} \ln(R_{11}n^-) \frac{\partial g(t)}{\partial l}\right] + R_{12}\left[\frac{\partial^2 g(t)}{\partial l\, \partial E_l}\right. \\ & \left. + \frac{\partial}{\partial l} \ln(R_{12}n^-) \frac{\partial g(t)}{\partial E_l} + \frac{\partial}{\partial E_l} \ln(R_{12}n^-) \frac{\partial g(t)}{\partial l}\right] \\ & + R_{22}\left[\frac{\partial^2 g(t)}{\partial E_l^2} + \frac{\partial}{\partial E_l} \ln(R_{22}n^-) \frac{\partial g(t)}{\partial E_l}\right] \end{aligned} \tag{27}$$

The derivation(35) shows that the reaction coefficients $R(l, E_l)$ should behave asymptotically as $R_{ij}(l, E_l) \rightarrow_{l\rightarrow\infty} \hat{R}_{ij}l^r$. The critical reaction rates which follow from this equation can be estimated, apart from factors of order unity, by a scaling analysis. From Eq. (10) it then follows that the first two terms on the right-hand side of Eq. (27) [which correspond to Eq. (24)] give rise to a relaxation time $\propto\epsilon^{(2-r)\beta\delta}$, while the terms proportional to $R^{(1,2)}$ yield a time $\propto\epsilon^{(1-r)\beta\delta+1}$, and the last two terms yield a time $\propto\epsilon^{2-r\beta\delta}$. Since $\beta\delta > 1$, these additional contributions represent corrections to scaling only. This result has a very intuitive physical interpretation. Near the critical point it is the *order parameter* (and hence l) which dominates the critical behavior and thus is the variable which relaxes most slowly. Hence $g(l, E_l, t)$ relaxes first with respect to E_l to some "local equilibrium" characterized by l, while the relaxation with respect to l governs the asymptotic decay for large times. This consideration readily shows that the exponents Δ_{EE}, etc., of the relaxation time of energy, etc., should be equal to the exponent of the order parameter relaxation time $\Delta_{\mu\mu}$, with $\Delta_{\mu\mu} = (2 - r)\beta\delta$. Note also that the above arguments can readily be generalized to many cluster coordinates, and are valid a fortiori if the order parameter is conserved. A more subtle situation arises⁽³⁹⁾ if it is not the slowest relaxing quantity that is conserved, but rather another one, e.g., the energy. This case will be considered elsewhere.⁽³⁸⁾

3.3. Structural Phase Transitions and Cluster Waves

A model Hamiltonian commonly used to describe structural phase transitions is (see, e.g., Ref. 40)

$$\mathscr{H} = \frac{m}{2}\sum_i \left(\frac{d\mathbf{u}_i}{dt}\right)^2 + \frac{A}{2}\sum_i \mathbf{u}_i^2 + \frac{B}{4}\sum_{i\alpha} u_{i\alpha}^4 + \sum_{i\neq j,\alpha\beta} J_{ij}^{\alpha\beta} u_i^{\alpha} u_j^{\beta} + \lambda V + \mathscr{H}_L \qquad (28)$$

where $\mathbf{u}_i = \{u_{i\alpha}, \alpha = x, y, z\}$ is the displacement of an atom (or ion, respectively) of effective mass m relative to equilibrium lattice positions in the disordered phase, A and B are constants describing the (anharmonic) effective single ion potential, and the $J_{ij}^{\alpha\beta}$ are (harmonic) coupling constants between the displacements of different unit cells of the lattice labeled by i and j. The term $\mathscr{H}_L$ describes the degrees of freedom of the lattice that are not associated with the structural transition, and λV describes the coupling between these degrees of freedom and the $\{\mathbf{u}_i\}$. These last two terms are usually omitted in simplified treatments. Note that if the parameter $(\frac{1}{2}A + \sum_{j(\neq i)} J_{ij}^{\alpha\beta})$ is sufficiently large and negative, ferrodistortive ordering occurs at low enough temperatures $[\langle\psi\rangle = (1/N)\sum_i \langle u_{i\alpha}\rangle \neq 0]$. If $\sum_{j(\neq i)} J_{ij}^{\alpha\beta}$ is positive, but A negative, we get antiferrodistortive ordering

$$\left\{\langle\psi\rangle = \frac{1}{N}\sum_i [\exp(i\mathbf{Q}\mathbf{R}_i)]\langle u_{i\alpha}\rangle \neq 0, \mathbf{Q} \neq 0\right\}$$

Note that in the limit $-A \to +\infty$, $B \to +\infty$, $-A/B = C = \text{const}$, and $J_{ij}^{\alpha\beta} = -(1/C)J_{ij}\,\delta_{\alpha x}\,\delta_{\beta x}$, Eq. (28) reduces to the Ising model [Eq. (22) with $H = 0$], if we introduce $\mu_i = u_{ix}/\sqrt{C}$ $(= \pm 1)$ and omit the kinetic energy term, which then becomes irrelevant. Thus the kinetic Ising model of Section 3.2 is a limiting case of the more general Hamiltonian, Eq. (28).

In the case where A and B stay finite, Eq. (28) obviously results in phonon excitations which are damped due to the anharmonic term. Since a phonon with frequency $\omega_{\mathbf{q}}$ represents a propagating mode of small displacements $\{u_i\}$, which are correlated for not too strong damping over at least the distance of a wavelength $2\pi/q$, and since we have introduced clusters to describe correlated order parameter fluctuations, we also have to associate propagating clusters with phonons. We may associate the cluster velocity v_l with the group velocity of a phonon wave packet, and the width Δq of the packet with the inverse cluster linear dimension $V_l^{-1/d}$. Since in large clusters as shown in Fig. 1 the displacement is actually very small, their propagating motion should be fully accounted for by phonons and their interactions. For simplicity, we consider the case of acoustic phonons only (i.e., structural transitions in A-15 compounds).

The kinetic energy of a moving cluster would simply be $m_l v_l^2/2$ for "droplets" at liquid–gas transitions. At structural phase transitions where the order parameter represents displacements we have instead (if the cluster propagation were due to optical phonons, this expression would be different(38))

$$E_t = \tfrac{1}{2}M \int_{V_l} d\mathbf{r}\, [d\psi(\mathbf{r})/dt]^2 = \tfrac{1}{2}Mv_l^2 \int_{V_l} d\mathbf{r}\, |\mathrm{grad}\, \psi|^2 \tag{29}$$

where M is an effective mass. Equating this energy with $dk_BT/2$ according to the classical equipartition theorem, we find an average velocity $\bar{v}_l$ of clusters given by

$$\bar{v}_l^2 \approx k_BT\xi^{2-d}\psi_\xi^{-2}M^{-1} \tag{30}$$

for clusters of size ξ, where $\psi_\xi \propto |T - T_c|^\beta$ is the typical order parameter variation due to such clusters.

The cluster concentration $\bar{n}_l(\mathbf{x}, t)$ will now change by three mechanisms: (i) the cluster reactions, $[\partial \mathbf{n}_l(t)/\partial t]_R = n_l L \mathbf{n}_l(t)/n_l$, with the Liouville operator L given by Eq. (24) for freely relaxing order parameters; (ii) the random cluster diffusion, $[\partial \bar{n}_l(t)/\partial t]_D = D_l\, \nabla^2 \bar{n}_l(t)$; and (iii) the cluster inertial propagation, $[\partial \bar{n}_l(t)/\partial t]_P = -\bar{v}_l\, \nabla \bar{n}_l(t)$. Thus, after a thermal average over the cluster velocities $\bar{v}_l$, one may generalize Eq. (24) for the Fourier components $g_l(\mathbf{q}, t)$ of the relative deviations of $\bar{n}_l(t)$ from equilibrium as

$$\frac{\partial^2 g_l(\mathbf{q}, t)}{\partial t^2} = \frac{\partial}{\partial t}\, [Lg_l(\mathbf{q}, t) - D_l q^2 g_l(\mathbf{q}, t)] - v_l^2 q^2 g_l(\mathbf{q}, t) \tag{31}$$

A detailed mathematical discussion of this cluster reaction-diffusion-propagation equation will be given elsewhere(38); here we restrict ourselves to a qualitative discussion of its physical consequences, in particular of its eigenvalues Λ appearing in $\exp(-\Lambda t)$ factors in the solutions for $g_l(\mathbf{q}, t)$ of Eq. (31):

(i) If the order parameter is not conserved, the reaction term gives a nonvanishing relaxation rate at zero wave vector (for explicit examples see Section 4). If the order parameter is conserved, as happens in the ferrodistortive case when the coupling terms λV in Eq. (28) are omitted, the lowest eigenvalue Λ_0 of the operator L must be zero.(38)

(ii) Close to T_c the diffusive term gives only a small correction $\propto q^2$ to the nonzero eigenvalues Λ in the case of a freely relaxing order parameter. For a conserved order parameter, the (Dq^2) correction to the lowest eigenvalue Λ_0 is more important, since this eigenvalue vanishes for $q = 0$.

(iii) The propagation term $v_l^2q^2$ leads to sound waves, as in the Boltzmann equation for a gas of "molecules" (corresponding to our "clusters") coupled by a scattering term $Lg_l(\mathbf{q}, t) - D_lq^2g_l(\mathbf{q}, t)$. It turns out(38) that for nonconserved order parameter the eigenvalues Λ of L stay real for small q (i.e., one has central peaks). However, for larger wave vectors, the smallest eigenvalues become complex, corresponding to damped propagating modes. For a conserved order parameter, the lowest eigenvalue is always complex, due to combined action of propagation (imaginary part) and diffusion (real part)(38)

$$\Lambda_0 = \pm ivq + Dq^2 + Q(q^3) \tag{32}$$

where

$$v^2 = \int_0^\infty l^2\bar{v}_l^2n_l\,dl \Big/ \int_0^\infty l^2n_l\,dl \tag{33}$$

analogous to Eq. (26) for D. Since the physical situation considered in this treatment is that of a structural transition where the modes associated with ferrodistortive ordering are acoustic, it seems reasonable to assume that Eq. (32) corresponds to this mode. Note that we have obtained frequency $\propto q$ and damping $\propto q^2 \propto$ (frequency)^2. No central peak in the structure function is obtained in this case, indicating that a treatment where energy conservation is neglected (since we treat our cluster concentrations as "isothermal") may be incomplete. This fact is also evident from a discussion of the liquid–gas transition, where this picture of thermally moving clusters has of course been used for a long time.[11] In the liquid–gas case the energy conservation gives rise to a central peak whose width is determined by the heat conductivity.

It is obvious from this discussion that conservation laws for order parameter and energy are of crucial importance for the eigenvalue spectrum of the cluster dynamics and thus for the peaks in the response functions, and in particular for the wave vector dependence of these quantities. This fact was overlooked in Krumhansl and Schrieffer's(7) treatment of clusters in a one-dimensional model, and relaxation at $\mathbf{q} = 0$ instead of diffusion was predicted, due to the incorrect approximation immediately before their Eq. (60). Of course, one-dimensional models have to be considered with caution for other reasons, too: The surface energy of a cluster is independent of the size of the cluster, in contrast to what happens at higher dimensionality. Therefore well defined clusters of the type shown in Fig. 1b occur in one dimension at any temperature, and the difference in order parameter between a cluster and its environment is of the order of $\langle u_i^2\rangle^{1/2}$ at any temperature. Since the ratio of $\langle u_i^2\rangle^{1/2}/a$, where a is the lattice spacing, is in general not a small number,

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[11] See, e.g., Ref. 41; for "heterophase" and "homophase" fluctuations see Ref. 42.

the phonon approximation is particularly bad in this case. In higher dimensionalities the difference between the order parameter of a domainlike cluster and its environment is of the order of $\epsilon^{\beta}\langle u_i^2\rangle^{1/2}/a$, which becomes arbitrarily small in the critical region: Therefore the arguments of Krumhansl and Schrieffer that these domains cannot be represented effectively by the usual phonon perturbation expansion are then not really conclusive.

Recent molecular dynamics studies(6,7,9) have given at least qualitative evidence for the existence of "cluster waves." We think that quantitative predictions(9) have to be considered with care, however: (i) The effect of errors due to intrinsic time correlations in finite time-averaging(43) has not been found appropriately discussed. (ii) Rather than in the microcanonic ensemble, where the total energy would be conserved, most of the computations are done in an ensemble where each individual atom is kept at constant temperature. This device may be considered as a strong coupling term λV in Eq. (28), which may also give rise to a central peak. (iii) Due to rounding errors in the machine computations, all quantities exhibit additional spurious relaxation on large time scales. Even if it is true that these effects are negligible in the case of a system of harmonic oscillators where one may make a comparison with the exact solution, these effects may be more important in a strongly anharmonic system close to its phase transition.

4. EXPLICIT CALCULATION OF RELAXATION FUNCTIONS FOR ANISOTROPIC MAGNETS

4.1. Reduction to an Eigenvalue Problem and Exactly Soluble Cases

We now consider the solutions of Eq. (24) for the case where the order parameter is not conserved (anisotropic magnets, Glauber model) and $\mathbf{q} \to 0$. It has been shown(13) that the diffusive term in Eq. (24) then yields only unimportant corrections to the leading singularities. The remaining equation, which can be rewritten as

$$\frac{d}{dt} g_l(0, t) = L_l g_l(0, t), \qquad L_l \equiv \frac{1}{n_l}\frac{d}{dl} R_l n_l \frac{d}{dl} \tag{34}$$

can be solved formally in terms of an eigenfunction expansion(13)

$$g_l(0, t) = \sum_{k=0}^{\infty} c_k \psi_k(l) e^{-\Lambda_k t}, \qquad L_l \psi_k(l) = -\Lambda_k \psi_k(l) \tag{35}$$

Here the expansion coefficients c_k are determined from the initial condition (cf. Section 3.1), while the spectrum of the eigenvalues Λ_k and associated eigenfunctions ψ_k are determined from Eq. (35) together with the boundary conditions for $l = 0$ and $l = \infty$. This could be done explicitly in two very special cases only, however(13): (i) using the Fisher model [Eq. (17)] at the critical isotherm and $r = 1$ (i.e., $\Delta_{\mu\mu} = \beta\delta$, which is bad approximation for $d = 3, 4$), where

$$\Lambda_k = \hat{R}h(k + 2 + 1/\delta), \qquad k = 0, 1, 2,... \tag{36}$$

and (ii) using the Fisher model at the coexistence curve and $\Delta_{\mu\mu} = (2 - r)\beta\delta = 1$ (i.e., mean-field dynamic exponents), where

$$\Lambda_k = [\hat{R}a\epsilon/(\beta\delta)^2](k + 3 - \alpha), \qquad k = 0, 1, 2,... \tag{37}$$

The associated eigenfunctions are generalized Laguerre polynomials in both cases, and the relaxation functions [Eq. (21)] can be expressed as hypergeometric functions.(13) It seemed doubtful to what extent these results are consequences of the special assumptions, however: In the one-dimensional Glauber model at $h = 0$ it is possible(44) to solve directly the equation $(d/dt)|\psi\rangle = L|\psi\rangle$, which corresponds to the master equation [Eq. (23)], and obtain the eigenvalues and eigenstates $|\psi\rangle$ of the exact "Liouville" operator L. In this case a *continuous* rather than a discrete eigenvalue spectrum is obtained.(44) In order to check to what extent the exact solutions [Eqs. (36) and (37)] are characteristic for the behavior of the system in the general case, and in order to obtain reliable information on $\phi_{\mu\mu}(0, t)$ for $d = 3$—which is the quantity of interest for experimental applications—numerical solution of Eq. (34) is necessary. Two techniques have been used: a matrix method and direct integration of Eq. (34).[12]

4.2. Matrix Method for the General Eigenvalue Spectrum

Replacing differentials dl by differences Δl with $\Delta l \gg 1$ but $\Delta l/l_\xi \ll 1$, we find that Eq. (34) is transformed to a coupled set of linear equations. Since the number of equations N_{eq} would still be infinite, it is necessary to truncate this set at some $l_{\max}$, with $l_{\max}/l_\xi \gg 1$. Then the eigenvalue problem [Eq. (35)] reduces to the standard problem of diagonalizing an $N_{\text{eq}} \times N_{\text{eq}}$ matrix. A special problem arises from the fact that a linear set of N_{eq} equations can have only N_{eq} eigenvalues, rather than the infinite number as found in Eqs. (36) and (37). In view of the fact that in Eqs. (36) and (37) the "density" of eigenvalues $d\Lambda_k/dk = \Lambda_k - \Lambda_{k-1}$ is a constant, it is impossible to approximate the full spectrum reasonably. We chose standard methods(46) which are known to yield good approximations for the lower part of the eigenvalue spectrum. We tested these methods in our model by applying them to the exactly soluble cases and trying several values of N_{eq}. For $N_{\text{eq}} = 80$, it turns

[12] More details on the numerical techniques and results can be found in Ref. 45.

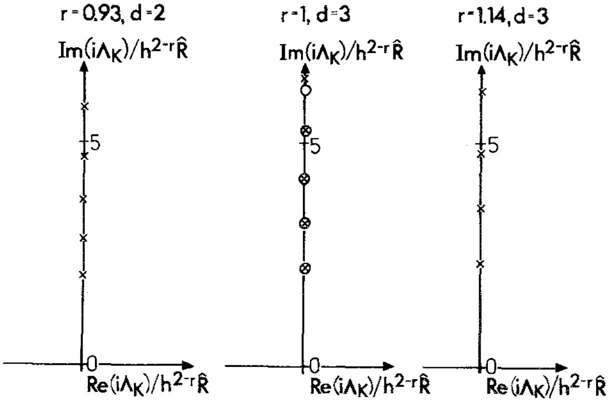

Fig. 2. Lowest part of the eigenvalue spectrum of the Liouville operator L at the critical isotherm for various values of the cluster reaction rate exponent r. The crosses denote the numerical results and the circles are the exact solution of Ref. 13.

out that Λ_0 is accurate to 2%, while the inaccuracy of Λ_1 is 14% and that of Λ_2 is 33%. For $N_{\text{eq}} = 120$, the respective numbers are one order of magnitude better and with $N_{\text{eq}} = 200$ the inaccuracy of Λ_0 is smaller than 10^{-3}, while even Λ_4 is accurate to a few percent. With this fine mesh, then, the eigenvalues have been evaluated for cases other than the two exactly soluble problems, as shown in Fig. 2. There the five lowest-lying eigenvalues are shown, still using the Fisher model at the critical isotherm, but allowing for different values of the exponent r. It is seen that the spectrum stays discrete, and also the magnitude of the "critical amplitude" of the lowest eigenvalue changes only very little with r. The only change in the spectrum of which we are aware is that for $r = 1$ the density $d\Lambda_k/dk$ does not remain constant. The systematic inaccuracy of the eigenvalues for larger k prevents us from giving any approximate relationships for Λ_k as a function of k, however.

Calculations similar to Fig. 2 have been performed also at the coexistence curve, and nonzero values of both h and ϵ have also been tried. Moreover, the improved assumption of Reatto and Rastelli[34] [Eq. (18)] instead of that of Fisher[15] [Eq. (17)] has been used. On the basis of these results we conclude that the eigenvalue spectrum of Eq. (34) is always discrete, except at the critical point $T = T_c$, $H = 0$: Since all eigenvalues scale with the same factor $\epsilon^{\Delta_{\mu\mu}}$ or $h^{\Delta_{\mu\mu}/\beta\delta}$, respectively, the eigenvalues merge at the critical point to form a continuous spectrum. We also find that the amplitudes of the lowest-lying eigenvalues depend only very little on the type of droplet model used, and on other adjustable parameters in the problem.

Finally, we comment on the question of why we find discrete spectra for zero wave vector, apart from the critical point, while the spectrum of the exactly solved one-dimensional Glauber model forms a single, continuous band. We start from the fact that Eq. (34) or Eq. (24) is continuum approximation to a discrete problem [Eq. (23)], which becomes asymptotically exact as $l \to \infty$, $|\epsilon| \to 0$, and $h \to 0$. The natural frequency scale in our problem is set by $\Omega = \langle W(\mathbf{x} \to \mathbf{x}') \rangle^{-1}$. The spectrum of eigenvalues Λ_k is quasicontinuous on this scale: In any interval Δl there is an arbitrarily large number of eigenvalues in the limiting case. Eigenvalues Λ_k such that $\Lambda_k \gg \Omega$ (i.e., for $k \to \infty$) are unphysical, of course, since the system cannot relax quicker than when spins are flipped without restrictions. If one could solve the cluster dynamics equations where differences $(l - l')$ are not yet replaced by differentials and other cluster coordinates included, one probably would get a continuous eigenvalue band at any temperature, the band gap going to zero for $T \to T_c$. A solution to this more complicated problem could be given in one dimension only.(47)

4.3. Numerical Integration of the Differential Equation

In this approach one replaces both differentials dl and dt by differences Δl and Δt, $1 \ll \Delta l \ll l_\xi$, and solves the resulting discrete initial value problem. In order to have stability of the standard integration routines,(48) one also has to require $\Delta t/\tau_\xi < \Delta l/l_\xi$ in our case, with $\Delta t/\tau_\xi \to 0$ and $\Delta l/l_\xi \to 0$. Here we use $\tau_\xi = (\beta\delta)^2 \hat{R}^{-1}(b\epsilon)^{-\Delta_{\mu\mu}}$ at the coexistence curve and $\tau_\xi = \hat{R}^{-1} h^{-\Delta_{\mu\mu}/\beta\delta}$ at the critical isotherm. This method is quite sensitive to the boundary conditions chosen for the cutoff $l_{\max}$. We obtained a reasonable behavior requiring that $g_{l_{\max}}(t) = 2g_{l_{\max}-\Delta l}(t) - g_{l_{\max}-2\Delta l}(t)$. Again the numerical routines were checked by comparison with the exactly soluble cases. It was found that a choice of $\Delta t/\tau_\xi = 0.005$ and $\Delta l/l_\xi = 0.025$ is sufficient to obtain both $\phi_{\mu\mu}(0, t)$ and $\phi_{E\mu}(0, t)$ with an accuracy of better than 3% for $t_s \equiv t/\tau_\xi \lesssim 0.5$.

Figure 3 displays some of the results obtained where the Fisher model [Eq. (17)] was used at the critical isotherm for various values of r for both

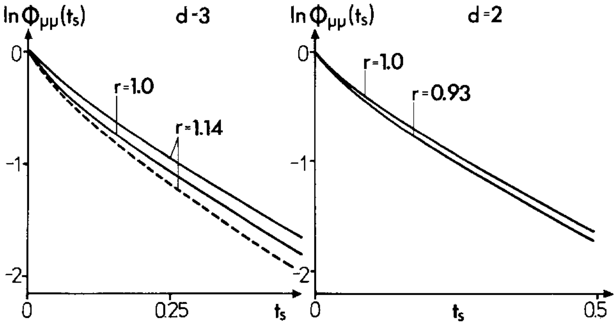

Fig. 3. Semilog plot of relaxation function $\phi_{\mu\mu}(0,t) = \phi_{\mu\mu}(t_s)$ versus scaled time t_s [$t_s = th^{2-r}\hat{R}$ at the critical isotherm and $t_s = t\epsilon^{\Delta_{\mu\mu}}\hat{R}a^{\Delta_{\mu\mu}}/(\beta\delta)^2$ at the coexistence curve]. Solid curves refer to the critical isotherm and dashed curves to the coexistence curve.

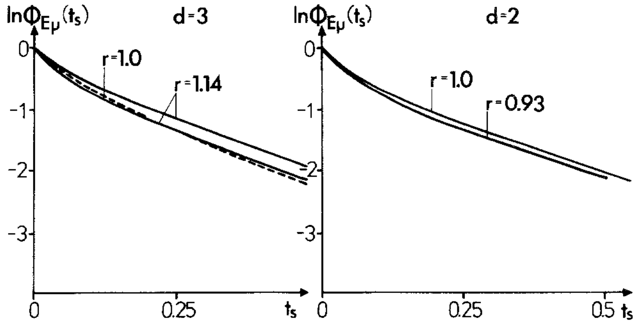

Fig. 4. Same as Fig. 3, for the energy relaxation function $\phi_{E\mu}(0, t) = \phi_{E\mu}(t_s)$.

$d = 2$ and 3. The choice $r = 0.93$ ($d = 2$) gives $\Delta_{\mu\mu} = 2.0$ and $r = 1.14$ ($d = 3$) gives $\Delta_{\mu\mu} = 1.31$, which are the values one expects from other methods.(36,39,49) It is seen that the order parameter relaxation function depends rather weakly on the value of r only. The same is true for $\phi_{E\mu}(0, t) \equiv \phi_{E\mu}(t_s)$ (Fig. 4). It is seen that $\phi_{E\mu}(t_s)$ deviates somewhat more strongly from an $\exp(-t_s)$ behavior than does $\phi_{\mu\mu}(t_s)$. We also include a few examples (dashed curves) of relaxation functions at the coexistence curve, to show that there is again no significant difference. In fact, most of the differences between the various relaxation functions seen in Figs. 3 and 4 are due to the difference in critical amplitude of the relaxation time.

The rather complicated eigenfrequency spectrum (Fig. 2) still leads to peaks in the dynamic susceptibility (Fig. 5), which resemble a Lorentzian line shape very closely. This illustrates that experimentally it will be rather

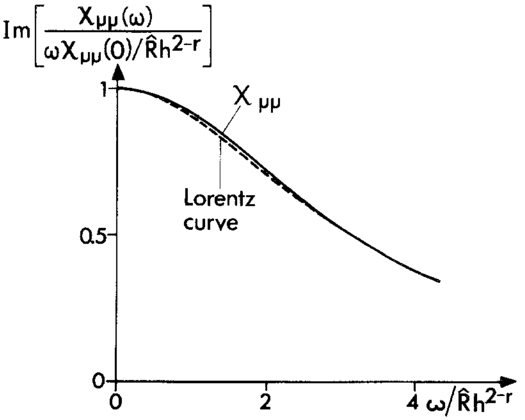

Fig. 5. Frequency-dependent susceptibility (for $q \to 0$) shown as a function of scaled frequency for $d = 3$ at the critical isotherm and $\Delta_{\mu\mu} = 1.31$. The dashed curve is a Lorentz function with the same half-width.

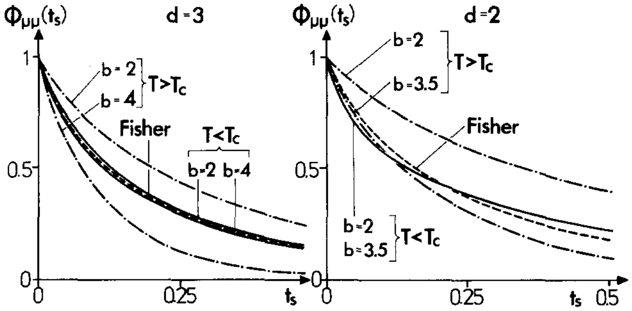

Fig. 6. Order parameter relaxation functions plotted vs. scaled time for the case of the cluster model of Reatto and Rastelli, for two values of the parameter b. Solid curves refer to $T < T_c$, dashed curves give the corresponding results based on the Fisher model, and dash-dotted curves refer to $T > T_c$. All curves are calculated at $h = 0$.

hard to reveal the correct eigenfrequency spectrum—usually one will be able to fit experimental data with a single Lorentzian line with some effective linewidth. These findings justify usual experimental procedures.

While the above examples are all based on the Fisher cluster model [Eq. (17)], Fig. 6 gives similar results where the model of Reatto and Rastelli [Eq. (18)] was used, which has the important advantage that it is applicable above T_c as well as below T_c, while the Fisher model makes sense below T_c only. Equation (18) contains an additional adjustable parameter b (the other constants are obtained by fitting the critical amplitudes of the order parameter at the coexistence curve and critical isotherm; see Ref. 16). But Fig. 6 demonstrates that for $T < T_c$, $\phi_{\mu\mu}(t_s)$ is nearly independent of b in the range of possible values for this parameter (see Ref. 34), and it is also hardly different from the treatment based on the model of Fisher. The same observation holds for $\phi_{E\mu}(t_s)$ as well. For $T > T_c$ a rather strong dependence on b is found. Since in the computer experiments of Stoll *et al.*⁽³⁶⁾ it was found that the critical amplitude of the relaxation time above T_c is about eight times larger than below T_c, clearly values of $b \approx 2$ have to be preferred. We thus conclude⁽⁴⁵⁾ that numerical calculations confirm the qualitative properties postulated in Ref. 13 but proven there only for special cases: The cluster reaction equation leads to a discrete eigenvalue spectrum and thus to deviations from a simple $\exp(-\text{const} \times t)$ decay, with the same critical exponents for the various relaxation functions of energy and order parameter.

5. NONLINEAR RESPONSE AND NONLINEAR RELAXATION FUNCTIONS

In this section we are concerned with the case of field changes Δh (or temperature changes $\Delta\epsilon$) such that $\Delta h/h$ (or $\Delta h\epsilon^{-\beta\delta}$, $\Delta\epsilon/\epsilon$, or $\Delta\epsilon h^{-1/\beta\delta}$) is *not* infinitesimally small. In this case the nonequilibrium relaxation functions defined in Eq. (20) differ from the thermal equilibrium relaxation functions [Eq. (21)] which describe the linear response. We first discuss the formal theory of nonlinear slowing down, and then our numerical results. In the following we denote the changes Δh, $\Delta\epsilon$, etc., by Δe.

5.1. General Theory of Nonlinear Critical Slowing Down

If we describe the state of the system $\{\mathbf{x}\}$ at time t by a density matrix $\rho(t)$, we can rewrite Eq. (23) as

$$-(d/dt)\rho(t) = L\rho(t), \qquad \rho(t) = \exp(-Lt)\,\rho(0) \tag{38}$$

where the exact "Liouville operator" L can be expressed in terms of the transition probabilities W. It is convenient to introduce the reduced density matrix $\phi(t)$ by

$$\rho(t) = \phi(t)\rho_\infty \tag{39}$$

where ρ_∞ is the thermal equilibrium density matrix of the final state reached for $t \to \infty$ after the change. It has been shown(36,51) that $\phi(t)$ satisfies also a Liouville equation [Eq. (38)], but with L replaced by another operator L' which is also linear and Hermitian,(36,51) and hence has the eigenvalue equation

$$L'|n\rangle = \Lambda|n\rangle, \qquad \Lambda \geqslant 0 \tag{40}$$

the eigenstates $|n\rangle$ forming a complete and orthonormal set. The time evolution of any $\mathbf{q}$-independent quantity $\langle A(t)\rangle$ is then given by(36,51)

$$\langle\delta A(t)\rangle = \operatorname{Tr}\rho_0 e^{-L't}\delta A(0), \qquad \delta A(t) = A(t) - \langle A(t=\infty)\rangle \tag{41}$$

where ρ_0 is the density matrix corresponding to the initial (thermal equilibrium) state. With the help of Eq. (40), Eq. (41) is found as

$$\langle\delta A(t)\rangle = \sum_n \operatorname{Tr}\rho_0|n\rangle\langle n|e^{-\Lambda t}\delta A(0) = \int_{\Lambda_0}^{\Lambda_c} A_\Lambda(\Delta e)f(\Lambda)e^{-\Lambda t}\,d\Lambda \tag{42}$$

where the sum over the eigenstates was rewritten as an integral over the eigenvalue spectrum, $f(\Lambda)$ being the density of eigenvalues (which reduces to a sum of delta functions if the spectrum is discrete). For $T \neq T_c$ we have $\Lambda_0 \neq 0$ and Λ_c finite (Λ_c being given by the relaxation of independent spins). The expansion coefficient A_Λ depends on the choice of the initial state, of course, and hence on Δe, while $f(\Lambda)$ is independent of the initial state. Remembering that in the limit $\Delta h/h \to 0$ (or $\Delta h\epsilon^{-\beta\delta} \to 0$, etc.) the nonequilibrium relaxation function $\langle\delta A(t)\rangle/\langle\delta A(0)\rangle$ reduces to an equilibrium relaxation function,(36) it is clear that the spectrum $\{\Lambda\}$ of L' describes the spectrum of the decay of any fluctuations at the final thermal equilibrium. Thus we must have

$$\Lambda_0 = \hat{\Lambda}_0 \epsilon^{\Delta_{\mu\mu}},\ \ \epsilon \to 0,\ \ h = 0; \qquad \text{or} \qquad \Lambda_0 = \hat{\Lambda}_0' h^{\Delta_{\mu\mu}/\beta\delta},\ \ h \to 0,\ \ \epsilon = 0 \tag{43}$$

Further, in order to have "extended dynamic scaling" (i.e., dynamic scaling holds for arbitrary operators A), we must require for all ϵ or h

$$f(\Lambda) = (1/\Lambda_0)\tilde{f}(\Lambda/\Lambda_0) \tag{44}$$

where $\tilde{f}$ is independent of ϵ and h.

We suppose now that the thermal equilibrium critical behavior of A is described by

$$\langle A\rangle_T - \langle A\rangle_{T_c} \propto \epsilon^a, \qquad a > 0 \tag{45}$$

e.g., $a = \beta$ if A is the magnetization, while $a = 1 - \alpha$ if A is the energy, etc. Then it is plausible that the expansion coefficients $A_\Lambda(\Delta e)$ satisfy static scaling (this is trivially true in the limit $\Delta h/h \to 0$, etc.), which can be put in the form

$$A_\Lambda(\Delta e) = \Lambda_0^{a/\Delta_{\mu\mu}} \tilde{A}(\Lambda/\Lambda_0, \Delta e/{\Lambda_0}^z) \tag{46}$$

where z is the appropriate scaling exponent (e.g., if $\Delta e = \Delta h$ and $\epsilon = 0$, $z = \beta\delta/\Delta_{\mu\mu}$, etc.). We now define the nonequilibrium relaxation time τ_A of the quantity A as

$$\tau_A = \int_0^\infty \langle \delta A(t)\rangle \, dt/\langle \delta A(0)\rangle \tag{47}$$

Using Eqs. (42), (44), and (46), we can transform τ_A into

$$\begin{aligned}\tau_A &= \int_{\Lambda_0}^{\Lambda_c} A_\Lambda(\Delta e)\frac{d\Lambda}{\Lambda} f(\Lambda)\langle \delta A(0)\rangle^{-1} \\ &= \Lambda_0^{-1}\int_1^{\Lambda_c/\Lambda_0} \Lambda_0^{a/\Delta_{\mu\mu}} \tilde{A}\left(x, \frac{\Delta e}{{\Lambda_0}^z}\right)\tilde{f}(x)\,\frac{dx}{x} \\ &\quad \times \left[\int_1^{\Lambda_c/\Lambda_0} \Lambda_0^{a/\Delta_{\mu\mu}} \tilde{A}\left(x, \frac{\Delta e}{{\Lambda_0}^z}\right)\tilde{f}(x)\, dx\right]^{-1}\end{aligned} \tag{48}$$

Note that $\langle \delta A(0)\rangle$ stays finite at arbitrary values of ϵ and h even if $\Delta e \to \infty$. This fact requires that $\tilde{A}(x, \infty)$ is finite and nonzero at finite x. Hence in Eq. (48) we may replace $\tilde{A}(x, \Delta e/{\Lambda_0}^z)$ by $\tilde{A}(x, \infty)$ in the limit where $\epsilon \to 0$ or $h \to 0$, and if Δe is kept finite, in order to get the leading singularity correctly. Near thermal equilibrium, high eigenfrequencies, which correspond to small spatial extent of fluctuations, make a negligible contribution to the eigenfunction expansion $\tilde{A}(x, y)$ of any quantity A as $\epsilon \to 0$ and $h \to 0$, and hence $\tilde{A}(x, y) \to_{x\to\infty, y\to 0} 0$ strongly enough that the main contribution in the denominator in Eq. (48) comes from x of order unity and not from the cutoff Λ_c/Λ_0. Therefore the cutoff may be replaced by infinity in both the numerator and denominator; the denominator behaves as $\langle \delta A(0) \rangle \propto \Lambda_0^{a/\Delta_{\mu\mu}}$, and the equilibrium relaxation time is $\tau_A \propto \Lambda_0^{-1}$, i.e., its exponent is independent of A, as expected.

Concerning the nonequilibrium relaxation, we must distinguish two cases:

(i) The ratio $\Delta h/h$ (or $\Delta h \epsilon^{-\beta\delta}$, etc.) is not small but kept at a finite value ($\propto y$) as $h \to 0$ (or $\epsilon \to 0$, etc.). Then the above argument still goes through, although $\tilde{A}(x, y)$ is now a different function depending on y. Explicit examples for this situation can be found in Ref. 13.

(ii) It is Δh (or $\Delta\epsilon$) rather than $\Delta h/h$, etc., which is kept constant with h (or ϵ) $\to 0$, and thus $\Lambda_0 \to 0$. Then $\langle \delta A(0) \rangle$ is a *finite* and *nonzero* quantity. This means that the contribution of the denominator of Eq. (48) must cancel the $\Lambda_0^{a/\Delta_{\mu\mu}}$ factor. This is possible for small but arbitrary Λ_0 only if $\tilde{A}(x, y)\tilde{f}(x)$ has a power law behavior:

$$\tilde{A}(x, \infty)\tilde{f}(x) \underset{x\to\infty}{\propto} x^{a/\Delta_{\mu\mu}-1} \qquad \text{if} \quad a/\Delta_{\mu\mu} < 1 \tag{49}$$

But then it follows that the main contribution to the integral in the numerator does not come from the cutoff, since there is an extra $1/x$ factor in the integrand, but from x of order unity. Thus we have shown that

$$\tau_A \propto \Lambda_0^{-(1-a/\Delta_{\mu\mu})}, \qquad \tau_A \propto \epsilon^{-(\Delta_{\mu\mu}-a)} \tag{50}$$

The relations (50) contradict early conjectures of Suzuki(51) and Stoll *et al.*(36) but agree with conjectures based on (generalized) Ginzburg–Landau treatments,(52) high-temperature series expansions,(53) and the cluster dynamics treatment.(13) In addition, Suzuki(54) has pointed out why his earlier arguments(51) in favor of $\tau_A \propto \epsilon^{-\Delta_{\mu\mu}}$ were inconclusive.

5.2. Cluster Dynamics Treatment of Nonlinear Slowing Down

Whereas the previous results only required the final state to be in the critical region, we now also assume that the initial state is close to T_c. We start by considering an exactly soluble case in more detail. At the critical isotherm and $r = 1$, we have in the case of the Fisher model, from Ref. 13, Eqs. (62) and (A10a),

$$\begin{aligned}\phi_\mu^{\Delta H}(0, t) = {} & \exp\left[-\hat{R}ht\left(2 + \frac{1}{\delta}\right)\right] \\ & \times \left\{\sum_{m=1}^{\infty} \left(\frac{-|\Delta h|}{h}\right)^m {}_2F_1\left(2 + \frac{1}{\delta} - m, 1 + \frac{1}{\delta}, 3 + \frac{1}{\delta}, \exp(-\hat{R}ht)\right)\right\} \\ & \times \left\{[\langle \mu(0) \rangle - \langle \mu(\infty) \rangle] h^{-1/\delta} \frac{\Gamma(3 + 1/\delta)}{q_0}\right\}^{-1}\end{aligned} \tag{51}$$

Since ${}_2F_1(a, b, c, 0) = 1$, the sum in the numerator approaches $-(|\Delta h|/h)(1 + |\Delta h|/h)^{-1}$ for $t \to \infty$. For $|\Delta h|/h \to +\infty$ and large t the numerator thus approaches $\exp[-\hat{R}ht(2 + 1/\delta)]$, while for the denominator we use

$$\langle\mu(0)\rangle - \langle\mu(\infty)\rangle \approx D(h + |\Delta h|)^{1/\delta} - Dh^{1/\delta} \approx D|\Delta h|^{1/\delta} \tag{52}$$

Thus we get for $t \to \infty$

$$\phi_\mu^{\Delta H}(0, t) \propto (h/|\Delta h|)^{1/\delta} \exp[-\hat{R}ht(2 + 1/\delta)] \tag{53}$$

while Eq. (51) gives for $\Delta h/h \to 0$ the thermal equilibrium relaxation function

$$\phi_{\mu\mu}(0, t) \propto \exp[-\hat{R}ht(2 + 1/\delta)] \tag{54}$$

without this extra factor $(h/|\Delta h|)^{1/\delta}$. Integration over time shows that the equilibrium relaxation time $\tau_{\mu\mu} = \int_0^\infty \phi_{\mu\mu}(0, t)\, dt$ diverges as $\tau_{\mu\mu} \propto h^{-1}$ as $h \to 0$ at fixed $\Delta h/h$, while the nonequilibrium relaxation time $\tau_\mu^{\Delta H} = \int_0^\infty \phi_\mu^{\Delta H}(0, t)\, dt$ diverges as $\tau_\mu^{\Delta H} \propto h^{-(1-1/\delta)}$ as $h \to 0$ at fixed Δh. This is a special case of Eq. (50), since in our case ($r = 1$) we have $\Delta_{\mu\mu} = \beta\delta$ and $a = \beta$ since we consider the order parameter. The relation (53) illustrates the fact that the general scaling structure of the nonequilibrium relaxation function of the order parameter is

$$\phi_\mu^{\Delta H}(0, t) = \tilde{\phi}_\mu(th^{\Delta_{\mu\mu}/\beta\delta}, \Delta h/h) \xrightarrow[\Delta h \gg h]{} \left(\frac{h}{\Delta h}\right)^{1/\delta} \tilde{\phi}_\mu{}'(th^{\Delta_{\mu\mu}/\beta\delta}, \infty), \qquad \epsilon = 0 \tag{55a}$$

$$\phi_\mu^{\Delta H}(0, t) = \tilde{\phi}_\mu(t\epsilon^{\Delta_{\mu\mu}}, \Delta h/\epsilon^{\beta\delta}) \xrightarrow[\Delta h \gg \epsilon^{\beta\delta}]{} (\epsilon^\beta/\Delta h^{1/\delta})\tilde{\phi}_\mu''(t\epsilon^{\Delta_{\mu\mu}}, \infty), \qquad h = 0 \tag{55b}$$

where $\tilde{\phi}_\mu{}'(x)$ and $\tilde{\phi}_\mu''(x)$ are functions which decay like a simple exponential for $x \to \infty$, and the same structure holds also for $\phi_\mu^{\Delta T}(0, t)$. With respect to the energy, one instead has

$$\begin{aligned} \phi_E^{\Delta H}(0, t) &= h^{(1-\alpha)/\beta\delta}\tilde{\phi}_E{}'(th^{\Delta_{\mu\mu}/\beta\delta}), \qquad && \epsilon = 0 \\ \phi_E^{\Delta H}(0, t) &= \epsilon^{1-\alpha}\tilde{\phi}_E''(t\epsilon^{\Delta_{\mu\mu}}), && h = 0 \end{aligned} \tag{56}$$

and the same structure holds for $\phi_E^{\Delta T}(0, t)$. These results follow also from more general droplet model considerations.

As a further example we show in Fig. 7 an example for $\phi_\mu^{\Delta T}(0, t)$ at the coexistence curve in three dimensions, which was obtained by numerical solution of Eq. (36) as described in Section 4.3. Here $\epsilon^{-\beta}\phi_\mu^{\Delta T}(0, t)$ is plotted versus $t\epsilon^{\Delta_{\mu\mu}}$ for three values of $\Delta T/\epsilon T_c$. While for larger values of $t\epsilon^{\Delta_{\mu\mu}}$ these curves already approach the limiting scaling function $\tilde{\phi}_\mu''$ [Eq. (55)], the behavior at small $t\epsilon^{\Delta_{\mu\mu}}$ is different: The reason is that $\tilde{\phi}_\mu''(x) \propto x^{-\beta/\Delta_{\mu\mu}}$ for $x \to 0$, while $e^{-\beta}\phi_\mu^{\Delta T}(0, 0)$ is finite for any finite value of $\Delta T/\epsilon T_c$.

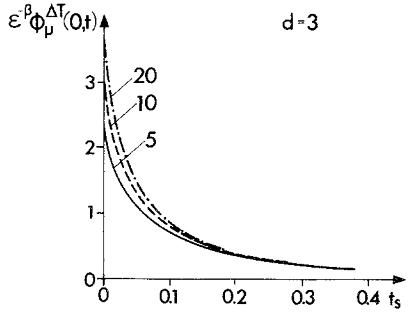

Fig. 7. Nonequilibrium relaxation functions $\phi_\mu^{\Delta T}(0, t)$ at the coexistence curve below T_c plotted versus scaled time. Parameter of the curves is $|\Delta\epsilon/\epsilon|$.

Thus the cluster reaction treatment is fully consistent with the general theory of Section 5.1 and proves scaling assumptions made there.

5.3. Computer Experiments on Nonlinear Slowing Down in the Two-Dimensional Glauber Model

The first Monte Carlo study of nonlinear slowing down by Ogita *et al.*(1) was consistent with $\tau_\mu^{\Delta T} \propto \epsilon^{-1.7}$ and $\tau_E^{\Delta T} \propto \epsilon^{-0.3}$; the large inaccuracy of these data obviously does not allow us to draw any firm conclusions concerning exponent estimates, however. The more accurate work of Stoll *et al.*(36) resulted in estimates $\tau_{\mu\mu} \propto \epsilon^{-1.85}$ and $\tau_\mu^{\Delta T} \propto \epsilon^{-1.85}$. However, the relative accuracy of these exponent estimates is 5–10%, and a substantial improvement of accuracy would require prohibitively more computing time due to the intrinsic difficulties of applying the Monte Carlo method at a critical point.(55) Therefore it is not surprising that the difference between $\Delta_{\mu\mu}$ and $\Delta_{\mu\mu} - \beta = \Delta_{\mu\mu} - 0.125$ did not show up clearly in the data.(55) Clearly more promising would be a study of $\tau_E^{\Delta T}$, since its exponent $\Delta_{\mu\mu} - (1 - \alpha) = \Delta_{\mu\mu} - 1$ differs much more drastically from the exponent of τ_{EE}, which is $\Delta_{EE} = \Delta_{\mu\mu}$. In Ref. 36 only τ_{EE} was calculated, not $\tau_E^{\Delta T}$. We have performed such a calculation for an 80×80 lattice of classical Ising spins (i.e., $s \to \infty$), where static properties were studied in some detail.(56) As initial state a completely ordered spin configuration was chosen, corresponding to a switch of temperature from 0 K to T. Figure 8 gives the results, and also shows data on the static susceptibility as a comparison. It is seen that roughly the correct asymptotic exponent of the susceptibility $\gamma = 1.75$ is observed in a temperature interval $0.1 \lesssim 1 - T_c/T \lesssim 0.5$, while at higher temperatures a different noncritical behavior sets in and at temperatures closer to T_c the critical divergence of the "statistical errors"(55) leads to estimates for the static susceptibility which are systematically too low, similar to what was observed in earlier calculations(36,57) in the $s = 1/2$ case. Therefore both the regimes $1 - T_c/T \gtrsim 0.5$ and $1 - T_c/T \lesssim 0.1$ had to be discarded also in the

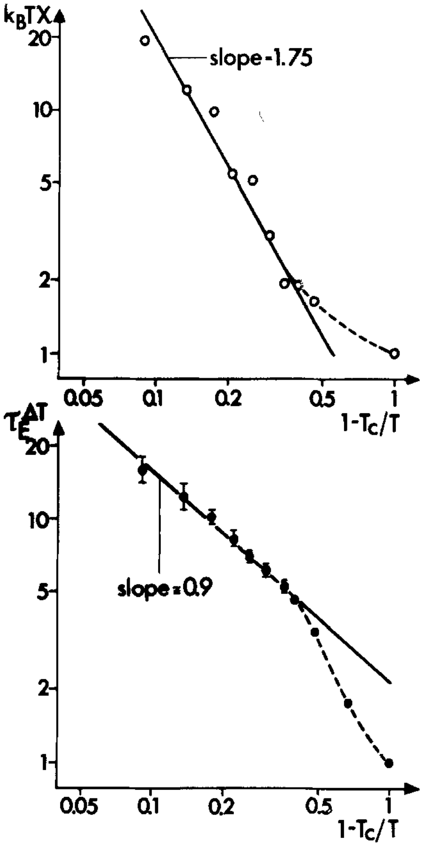

Fig. 8. Monte Carlo results (points) for the static susceptibility $k_BT\chi$ (upper part) and energy nonequilibrium relaxation function (lower part) of the classical kinetic Ising model on the square lattice. Times are expressed in units of Monte Carlo steps/spin.

calculation of $\tau_E^{\Delta T}$, to avoid systematic errors. From Fig. 8 it is seen that the estimate for the exponent of $\tau_E^{\Delta T}$ obtained by us is $\Delta_E^{\Delta T} \approx 0.9$, which is fairly consistent with the scaling estimate $\Delta_E^{\Delta T} = \Delta_{\mu\mu} - 1$ since$^{(39,49)}$ $\Delta_{\mu\mu} \approx 2$.

In a similar but independent recent study Bolton and Johnson$^{(58)}$ obtained $\Delta_E^{\Delta T} \approx 0.4$, which is comparable to the result of Ogita *et al.*$^{(1)}$ but disagrees with ours. We believe that these results are incorrect, however, since they are based on data closer to T_c, which are rather unreliable, since the statistics of their studies is not better than ours. In fact, close to T_c one expects statistical relative fluctuations of the energy in an $L \times L$ system which behave as $\epsilon^{-\alpha/2}L$ as $\epsilon \to 0$, while at the same time the scale of $\phi_E^{\Delta T}(0, t)$, where its main contributions comes from, is given by the factor $\epsilon^{1-\alpha}$ [cf. Eq. (56)], which goes strongly to zero as $\epsilon \to 0$. Reliable estimates of $\phi_E^{\Delta T}(0, t)$ are possible only as long as $\phi_E^{\Delta T}(0, t) \gg \epsilon^{-\alpha/2}/L$, i.e., $\epsilon \gg L^{-1}$ for two dimensions. This condition was overlooked in Refs. 1 and 58 and therefore the error of their estimates for $\Delta_E^{\Delta T}$ is very pronounced.

6. CONCLUSIONS

The aim of the present paper was an extension of the cluster reaction approach developed by Binder *et al.*,$^{(12-14)}$ in particular, applications to other physical systems and nonlinear slowing down. Our results include:

(i) Various possibilities of cluster pictures have been critically compared, and "fluctuation clusters" were defined in terms of a coarse-grained order parameter $\psi(\mathbf{r})$. "Clusters" are the fluctuations of this coarse-grained order parameter. The properties of very large clusters above and below T_c differ from each other, since large, domainlike fluctuations (Fig. 1b) are important only below T_c. (Thus an essential singularity for $h = 0$ should occur only below T_c, but not above T_c.) The consequences for dynamic properties may be more drastic (e.g., different velocity laws for cluster waves above and below T_c in models with propagating cluster modes, etc.).

(ii) Assuming that for models without energy conservation it is sufficient to use only one cluster coordinate (i.e., its excess of the order parameter, which is the slowest varying variable in the system), we have proposed a cluster reaction–diffusion–propagation equation. The reactions and diffusion of clusters lead to a damping of propagating cluster waves. In the limit where cluster waves are unimportant, the equation reduces to the reaction-and-diffusion equation studied before.$^{(12-14)}$

(iii) An extension of the treatment to include other cluster coordinates (like the cluster energy) has also been given, similar to the treatment of multicomponent nucleation theory.$^{(35)}$ We showed that in models without conservation laws the inclusion of such additional degrees of freedom does not affect the leading singularities in the dynamic response functions, but leads only to corrections to scaling.

(iv) The one-coordinate cluster reaction equation has been solved numerically for a variety of cases not accessible to exact solution. Its eigenvalue spectrum stays discrete in all these cases (except right at the critical point). The relaxation functions and dynamic susceptibilities are obtained by numerical integration in a variety of cases. Use of the droplet model of Reatto and Rastelli allows a treatment of both $T > T_c$ and $T < T_c$, while the Fisher model is restricted to $T < T_c$. We showed that the relaxation functions for $T < T_c$ in both models nearly coincide. This fact suggests that the calculated relaxation functions should be reasonable approximations to the actual exact function, since they do not depend strongly on the details of these approximative models. Numerically, however, the dynamic susceptibility is nearly indistinguishable from an ordinary Lorentzian, and hence the polydisperse nature of the relaxation can hardly be seen by scattering experiments, unfortunately.

(v) A general scaling theory of the nonlinear slowing down has been developed, which is *not restricted* to (inaccurate) generalized Ginzburg–

Landau assumptions like the approach of Racz, although it leads to the same scaling relations for the critical exponents of nonlinear slowing down. We emphasize the fact that this part of the treatment is far more general than the cluster model approach of the rest of the paper, although the cluster approach again leads to results which are a special explicit case of our general formalism. Numerical calculations of nonlinear relaxation functions have also been presented in the three-dimensional case. In principle, these results could be compared with quenching experiments(59) in the superstructure alloy Ni_3Mn. We did not attempt to perform this comparison, due to uncertainties in the activation energy for the atomic exchange process, which affect somewhat the accuracy of these results.(52) A meaningful comparison must await an independent determination of this activation energy. Nevertheless we strongly suggest that additional similar experiments be performed.

(vi) Monte Carlo results for the nonlinear slowing down of the energy have been presented, and are reasonably consistent with our theoretical predictions, although the data are restricted to temperatures not too close to T_c. The failure of other, similar Monte Carlo treatments(1,58) is traced back to the use of data too close to T_c where the dominant part of the energy relaxation function has the same magnitude as energy fluctuations in the finite sample. In order to obtain meaningful estimates in that temperature regime, considerably larger systems or better statistics would be required.

REFERENCES

1. N. Ogita, A. Keda, T. Matsubara, H. Matsuda, and F. Yonezawa, *J. Phys. Soc. Japan* (*Suppl.*) **26**:145 (1969).
2. L. P. Kadanoff, in *Critical Phenomena*, M. S. Green, ed., Academic, New York (1971), p. 118.
3. A. M. Gottlieb and P. Heller, *Phys. Rev. B* **3**:3615 (1971).
4. G. J. Adriaenssens, *Phys. Rev. B* **12**:5116 (1975); G. J. Adriaenssens, J. Bjorkstam, and J. Aikins, *J. Mag. Resonance* **7**:99 (1972).
5. R. L. Armstrong and C. A. Martin, *Phys. Rev. Lett.* **35**:294 (1975).
6. S. Aubry and R. Pick, *Ferroelectrics* **8**:471 (1974).
7. S. Aubry, Thesis, CEN, Saclay (1974), unpublished.
8. J. A. Krumhansl and J. R. Schrieffer, *Phys. Rev. B* **11**:3535 (1975).
9. T. Schneider and E. Stoll, *J. Phys. C* **8**:283 (1975); *Phys. Rev. B* **13**:1216 (1976).
10. B. J. Ackerson, C. M. Sorensen, R. C. Mockler, and W. J. O'Sullivan, *Phys. Rev. Lett.* **34**:1371 (1975).
11. F. Schwabl, in *Anharmonic Lattices, Structural Transitions and Melting*, T. Riste, ed., Leiden, Nordhoff (1974).
12. K. Binder, D. Stauffer, and H. Müller-Krumbhaar, *Phys. Rev. B* **10**:3853 (1974).
13. K. Binder, D. Stauffer, and H. Müller-Krumbhaar, *Phys. Rev. B* **12**:5261 (1975).
14. K. Binder and D. Stauffer, *Phys. Rev. Lett.* **33**:1006 (1974).
15. M. E. Fisher, *Physics* **3**:255 (1967).
16. E. Stoll, K. Binder, and T. Schneider, *Phys. Rev. B* **6**:2777 (1972); K. Binder and H. Müller-Krumbhaar, *Phys. Rev. B* **9**:2328 (1974).
17. K. Binder, *Ann. Phys.* (*N.Y.*) **98**: in press (1976).

18. H. Müller-Krumbhaar, *Phys. Lett.* **48A**:459 (1974); **50A**:27 (1974).
19. J. W. Essam, in *Phase Transitions and Critical Phenomena*, C. Domb and M. S. Green, eds., Academic, New York (1972), Vol. 2, p. 197.
20. L. P. Kadanoff, *Physics* **2**:263 (1966).
21. K. G. Wilson and J. Kogut, *Phys. Rep.* **12C**:75 (1974); K. G. Wilson, *Rev. Mod. Phys.* **47**:773 (1975).
22. J. S. Langer, *Physics* **73**:61 (1974).
23. A. I. Larkin and D. E. Khmelnitzkii, *Soviet Phys.—JETP* **29**:1123 (1969).
24. M. E. Fisher, *Rep. Prog. Phys.* **30**:615 (1967).
25. C. Domb and M. S. Green, eds., *Phase Transitions and Critical Phenomena*, Academic, New York (1972), Vols. 1–6.
26. P. G. de Gennes, P. Lafore, and J. P. Millet, *J. Phys. Chem. Solids* **11**:105 (1959).
27. K. Binder and D. Stauffer, *J. Stat. Phys.* **6**:49 (1972); C. Domb, T. Schneider, and E. Stoll, *J. Phys. A* **8**:L90 (1975).
28. C. Domb, *J. Phys. A* **9**:283 (1976).
29. C. K. Majumdar, *Phys. Rev. B* **10**:2857 (1974).
30. D. Stauffer, C. S. Kiang, and G. H. Walker, *J. Stat. Phys.* **3**:323 (1971).
31. B. I. Halperin and P. C. Hohenberg, *Phys. Rev.* **177**:952 (1969).
32. M. M. Bakri and D. Stauffer, preprint.
33. A. F. Andreev, *Soviet Phys.—JETP* **18**:1415 (1964).
34. L. Reatto and E. Rastelli, *J. Phys. C* **5**:2785 (1972).
35. K. Binder and D. Stauffer, *Adv. Phys.*, in press (1976).
36. E. Stoll, K. Binder, and T. Schneider, *Phys. Rev. B* **8**:3266 (1973).
37. L. van Hove, *Physica* **21**:517 (1955).
38. D. Stauffer and K. Binder, in preparation.
39. B. I. Halperin, P. C. Hohenberg, and S. K. Ma, *Phys. Rev. B* **10**:139 (1974).
40. T. L. Einstein and R. Cohen, *Phys. Rev. B* **7**:1932 (1973).
41. T. P. Tseng, S. K. Feng, C. Cheng, and W. Band, *J. Chem. Phys.* **8**:20 (1940); J. L. Katz, H. Saltsburg, and H. Reiss, *J. Colloid Interface Sci.* **21**:560 (1966).
42. J. Frenkel, *Kinetic Theory of Liquids*, Dover, New York (1946), Chapter VII.
43. R. Zwanzig and N. K. Ailawadi, *Phys. Rev.* **182**:280 (1969).
44. B. U. Felderhof, *Rept. Math. Phys.* **1**:215 (1971); **2**:251 (1971).
45. R. Kretschmer, *Diplomarbeit*, Universität Saarbrücken (1975), unpublished.
46. L. Collatz, *Eigenwertaufgaben mit technischen Anwendungen*, Akademische Verlagsges., Leipzig (1963), p. 355.
47. A. Baumgärtner and K. Binder, in preparation.
48. R. Richtmeyer and K. W. Morton, *Difference Methods for Initial Value Problems*, Interscience, New York (1967), p. 190.
49. H. Yahata, *J. Phys. Soc. Japan* **30**:657 (1971).
50. M. T. Hutchings, M. P. Schulhof, and H. J. Guggenheim, *Phys. Rev. B* **5**:154 (1972).
51. M. Suzuki, *Prog. Theor. Phys.* **42**, 1076 (1969); **43**, 882 (1970); *Int. J. Magn.* **1**, 123 (1971).
52. Z. Racz, *Phys. Rev. B* **13**:263 (1976); M. E. Fisher and Z. Racz, preprint.
53. M. F. Collins and Z. Racz, *Phys. Rev. B* **13**:3074 (1976).
54. M. Suzuki, preprint.
55. K. Binder, in *Phase Transitions and Critical Phenomena*, C. Domb and M. S. Green, eds., Academic, New York (1976), Vol. 5b, p. 1.
56. K. Binder and D. P. Landau, *Phys. Rev. B* **13**:1140 (1976).
57. D. P. Landau, preprint.
58. H. C. Bolton and C. H. Johnson, *Phys. Rev. B* **13**:3025 (1976).
59. M. F. Collins and H. C. Teh, *Phys. Rev. Lett.* **30**, 781 (1973).