Cluster statistics of the lattice gas model in three and two dimensions

H. Müller-Krumbhaar*

Institut für Festkörperforschung, Kernforschungsanlage Jülich, Jülich, West Germany †

E.P. Stoll

IBM Zurich Research Laboratory, 8803 Rüschlikon, Switzerland

(Received 21 July 1976)

Cluster statistics in the lattice gas system were evaluated in three dimensions ($d = 3$) below the critical point, and in two dimensions ($d = 2$) above T_c using a Monte Carlo method. Defining clusters as sets of l particles connected by nearest-neighbor bonds, we found remarkable deviation from semiphenomenologic cluster probability formulas below T_c. This deviation is attributed to the formation of spongelike noncompact macroclusters near the percolation temperature $T_p < T_c$. Above T_c the cluster probabilities in two dimensions may be scaled in the variable $\bar{l} = (1 - T_c/T)\, l^{\sigma}$ with $\sigma = 0.53$ below T_c. In contrast to the two-dimensional case of $T < T_c$ here the cluster formulas cannot explain the distribution up to clusters with $l \leq 2000$ particles. For $T \rightarrow \infty$ ($d = 2$) the cluster probability p_l decays as $p_l \sim \exp(-\text{const}\, l^{\zeta})$ with $\zeta \approx 1$ for sufficiently large l. This supports recent arguments that the Griffiths singularity for dilute systems is an essential one.

I. INTRODUCTION

Clustering of atoms is a well-known phenomenon in many topics of phase transitions,[1-16] although few precise details are known. Metallurgical examples are segregation and phase separation in alloys[5-7]; other examples are condensation and evaporation in liquid–gas systems[1-4] or magnetization reversal in ferromagnets.[8,12]

Many aspects of these first-order transitions are usually described by nucleation theory.[2,4,8-12] A microscopic foundation requires the definition of formation probabilities for large clusters (e.g., liquid droplets in the vapor phase). This probability is assumed to be proportional to $\exp(-G_l/k_BT)$, where G_l is a free energy for the formation of a cluster of l molecules. But the correct values of G_l as well as the pre-exponential factor of proportionality have been the subject of controversy for more than 20 years.[4,13]

We have made Monte Carlo studies on cluster statistics by direct determination of the equilibrium probabilities for the occurrence of clusters as a function of their size instead of calculating droplet free energies. It is then also irrelevant which of the thermodynamic potentials should be used for G_l, and we avoid the ambiguity in the pre-exponential factor.

For practical purposes we should like to simulate, for example, liquid droplets in coexistence with the vapor. However, the distance-dependent interaction energies[15] would make the calculations very time consuming. We therefore studied the temperature dependence of equilibrium cluster concentrations in the somewhat simpler model of a lattice gas,[16] which is also known as Ising model, having properties very similar to a liquid–gas system or a binary alloy. Near the critical temperature T_c, for example, the lattice gas model predicts the density difference between liquid and gas to vanish as $(T_c - T)^{\beta}$ along the coexistence curve with $\beta \approx 0.31$, while experiments[17] give $\beta = 0.32$. This Ising model is obviously in better agreement with real fluids than, for example, the van der Waals equation[18] where $\beta = 0.5$. Another advantageous property of the model is its analogy to ferromagnetic systems. "Vapor" then corresponds to "up" magnetization direction, and "liquid" corresponds to "down" magnetization. The equilibrium pressure in the fluid system corresponds to a zero external field in the magnetic system. Therefore, there is no additional parameter necessary to be adjusted to keep the system at the coexistence line. This avoids inaccuracies in the determination of the "bulk free energy" of condensation, which could be quite important in other models.

In order to have good statistics for large clusters, the Monte Carlo simulation was carried out for temperatures near the critical point, since at T_c the surface tension (nucleation barrier) of a cluster[19] vanishes. At our lowest temperature $T = 0.8\,T_c$, however, the cluster concentration is very small,[20] so that we expect our results to be meaningful for nucleation theory in general, not merely for nucleation near critical points. Of particular interest for the comparison with semiphenomenological droplet models are the temperatures $T \rightarrow T_c$ and $T \rightarrow \infty$. It is found that near T_c the cluster statistics may be fitted with homogeneous functions of appropriate scaling variables by introducing an additional critical exponent. This may account for different degrees of compactness of clusters in different systems. At $T = \infty$, our data confirm recent ideas[21] on an asymmetric behavior of randomly diluted ferromagnets near the percolation threshold.

In Sec. II we give a description of the droplet models. In Sec. III the results of the three-dimensional calculations are discussed. For the two-dimensional system this is done in Sec. IV, while Sec. V contains concluding remarks.

II. CLUSTER MODELS IN THE LATTICE-GAS SYSTEM

The lattice–gas or lattice model of a binary mixture[16] is defined as a lattice of dimensionality d which may be

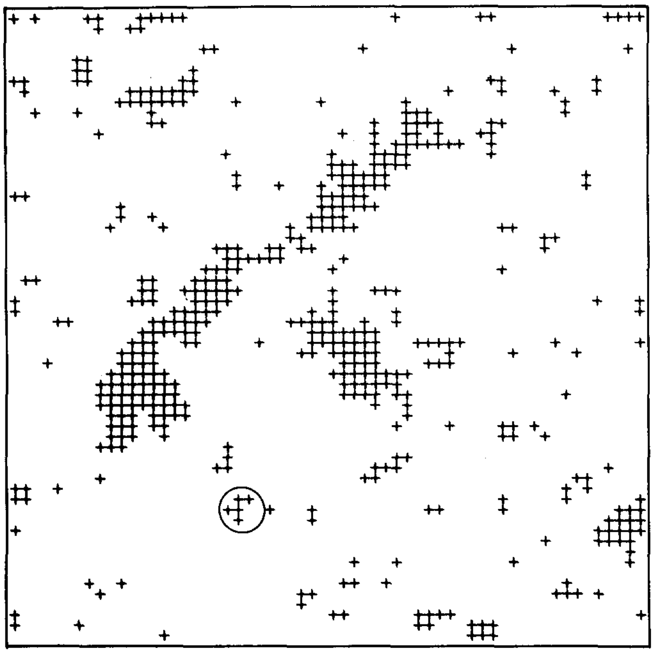

FIG. 1. Equilibrium clusters in a two-dimensional (60×60 sites) lattice–gas model. The circle surrounds an ($l=5$)-particle cluster.

partly filled with interacting particles either of type A or B (binary mixture). The Hamiltonian of the system is

$$\mathcal{H} = -\tilde{J} \sum_{\langle i,j\rangle} c_i c_j - \mu \sum_i c_i \,, \tag{1}$$

where $\tilde{J}$ is the interaction parameter, $c_i = \{0, 1\}$ is the concentration of particles "A" at site i, and μ is the chemical potential, the first sum going over all pairs of sites. An alternative description is in terms of "spin" variables $s_i \equiv 1 - 2c_i$:

$$\mathcal{H} = -J \sum_{\langle i,j\rangle} S_i S_j - \Delta\mu \sum S_i \,, \tag{2}$$

where $J = \tilde{J}/4$ and $(\Delta\mu/2)$ is the chemical potential difference between the $S_i = +1$ and $S_i = -1$ states, being zero at the coexistence line.

"Clusters" of particles are now easily defined as sets of identically occupied sites, which are connected by at least one nearest-neighbor bond. This is a rather unambiguous definition in contrast to models[15] with spatially continuously varying interaction potential, where a cutoff has to be introduced rather arbitrarily. An example for such clusters in a two-dimensional 60×60 lattice model as obtained by Monte Carlo simulation is shown in Fig. 1.

In the usual formulation of phenomenological models[1–4,13] of noninteracting clusters it is now assumed that the free energy of a cluster of one phase or component within the other component consists of a bulk part proportional to the number l of particles in the cluster, and of a surface part, which is for compact clusters proportional to $l^{(d-1)/d}$ in a d-dimensional system.

A phenomenological ansatz[19] for the Gibbs free energy of such a cluster is then, for example,

$$G_l/k_BT = -l\ln(y) + l^{\sigma}\ln(x) + \tau\ln l + C + \cdots \,. \tag{3}$$

The x- and y-terms (corresponding to surface and bulk free energy) contain constants which depend on the interaction parameters between particles, on temperature, and on external forces. The exponent σ represents the ratio of the exponents of the effective surface free energy over volume free energy [$\sigma = (d-1)/d$ in the d-dimensional spherical case]. The coefficients τ and C arise from entropy corrections, their magnitude and physical interpretation still being the subject of controversy.[13] The probability p_l that a particular site of the lattice is part of a cluster with l-connected particles accordingly is written as

$$p_l \sim \exp(-G_l/k_BT) \,, \tag{4}$$

or with Eq. (3)

$$p_l = q_0 l^{-\tau} \exp\left(-A(T)l^{\sigma} - \frac{\Delta\mu}{k_BT}\, l + \cdots\right) \,, \tag{5}$$

where q_0 is a constant, and $A(T)$ is a temperature-dependent function representing the surface free energy of a cluster, τ and σ being two exponents that allow the static scaling relations near the critical point to be fulfilled.

The expectation value for the concentration is then obtained by the sum rule

$$\langle c\rangle \equiv \tfrac{1}{2}(1 - \langle s\rangle) = \sum_{l=1}^{\infty} l p_l \,. \tag{6}$$

This now means that the partition function has been parametrized in terms of noninteracting clusters, leading to an essential singularity at the coexistence line $\Delta\mu \to 0$ [Eqs. (5) and (6)] for $\sigma < 1$, in accordance with the exact proof[22] that all thermodynamic derivatives exist at the coexistence line.

An explicit form for $A(T)$ turns Eq. (7) in the droplet model of Fisher[19]:

$$A(T) = a\left(\frac{J}{k_BT} - \frac{J}{k_BT_c}\right) \,, \tag{7}$$

where "a" is a constant. At T_c this term vanishes, while above it is no longer applicable owing to the exponent increasing with l^{σ}. As already mentioned by Fisher, this cluster model neglects the effects of excluded volume and the possibility of having noncompact large clusters. In fact, it is highly probable that large clusters of type-"A" atoms have smaller clusters of the "B" atoms inside. They can, therefore, be in some local equilibrium, and their contribution to the singular part of the free energy would be reduced. Reatto[23,24] suggested including a multiplicative factor in the formula, to be interpreted as the probability that the cluster be compact, to give p_l':

$$p_l' = p_l\{B\exp[-bA(T)l^{\sigma}] + 1\}^{-1} \,, \tag{8}$$

where $b \gtrsim 1$ is a constant, and B is independent of l but could have an analytic dependence upon temperature. Above T_c we have $A(T) < 0$, and therefore Eq. (8) is then also convergent for large l. There are several other propositions[25,26] for modifications of the Fisher model, which do not, however, apply above T_c. We shall therefore restrict ourselves to the simplest case at present.

The close similarity of the thermodynamic behavior of two-phase systems such as gas–liquid mixtures, binary alloys, and anisotropic ferromagnets is indicated by their similar behavior around the critical point.[17] It therefore appeared to be useful to evaluate cluster statistics also close to T_c; in addition, we expect better statistics for large clusters due to decreasing surface tension as T approaches T_c, and finally, there are detailed predictions from scaling theory,[16,27] which should be fulfilled by phenomenological cluster probability formulas. We therefore briefly summarize the predictions for critical behavior which will be tested by the Monte Carlo simulations.

The singular part of the free energy near the critical point in scaled form is expressed by a homogeneous function[27]

$$G=\lambda^{2-\alpha}\tilde{G}_0\left(\frac{\epsilon}{\lambda},\frac{h}{\lambda^{\Delta}}\right), \tag{9}$$

where λ is a free parameter, $\epsilon=(T_c-T)/T_c$ is the relative temperature difference, $h\equiv\Delta\mu/k_BT$, and α and Δ are "critical" exponents. The concentration $\langle c\rangle\equiv\frac{1}{2}(1-\langle s\rangle)$ is then obtained by taking the derivative

$$\langle s\rangle=\partial G/\partial h, \tag{10}$$

$$\lambda=\epsilon,\quad h=0:\ \langle s\rangle=m_\epsilon\epsilon^{\beta};\ \beta=2-\Delta-\alpha, \tag{11a}$$

$$\lambda^{\Delta}=h,\quad \epsilon=0;\ \langle s\rangle=m_h h^{1/\delta};\ \delta=\Delta/\beta, \tag{11b}$$

where m_ϵ and m_h are constants, Eq. (11a) holds for the coexistence line, and Eq. (11b) holds for the critical isotherm. The above-mentioned exponents in the Fisher model, Eqs. (5) and (7), are

$$\tau=2+1/\delta,\qquad \sigma=1/\beta\delta. \tag{12}$$

The prefactors q_0 and a are related to the proportionality constants m_ϵ, m_h of Eqs. (11a) and (11b).

These exponents of the cluster model should hold for clusters[28] up to a size $l\approx\xi^d$, where ξ is the characteristic length of correlation between particles in the lattice. For much larger clusters $l\gg\xi^d$ fluctuations of the surface are again of the order $\sim\xi$ and therefore become unimportant. Then the clusters become spherical and the surface exponent σ will be $\sigma=(d-1)/d$, as in classical nucleation theory.[13] For our model at a relative temperature $\epsilon=0.1$ we have $\xi=\xi_0 e^{-\nu}\approx 4.4$ (with the correlation-length exponent $\nu\approx 0.64$) and $l_\xi\approx\xi^d\approx 80$. Scaling theory should therefore be applicable at least in the region of clusters of this size. More detailed statements concerning this changeover from fluctuation-dominated to geometric regime can be found in Refs. 28–30.

III. THREE-DIMENSIONAL SYSTEM

Monte Carlo calculations[31] were carried out on a $30\times30\times30$ site lattice with periodic boundary conditions using standard procedures; the statistical averages were taken over $\approx 10^4$ MC trials/site. A special procedure was developed[32] to count clusters in the three-dimensional system. The MC method was tested by comparing the computed order parameter $\langle s\rangle$ with the results from scaling theory[16] (Fig. 2), the statistical errors were smaller than the dimension of the points (+) in Fig. 2. The errors of the magnetization were analyzed according to Ref. 31; unambiguous estimates for the errors of the cluster distribution could not be obtained owing to the time correlations involved. The cluster counting method was tested in three ways: A given set of clusters was analyzed; for arbitrary cluster distributions the sum rule, Eq. (5), was checked; and finally, 90° rotations of the system about its axes were checked to give identical results.

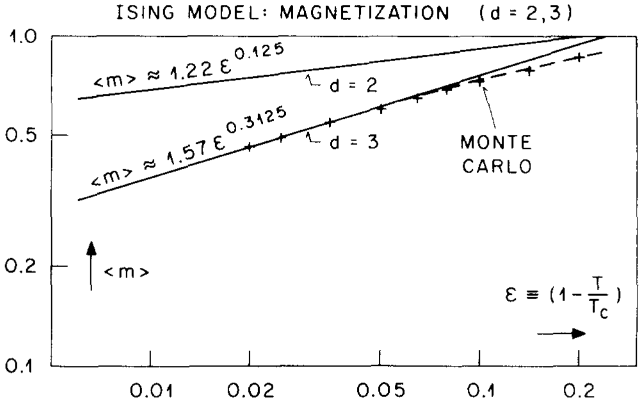

FIG. 2. Ising model near the critical temperature ($T<T_c$). The full lines give the asymptotic scaling behavior for two- and three-dimensional systems; the crosses + denote the Monte Carlo results as a test.

In Fig. 2 the order parameter $\langle m\rangle\equiv\langle s\rangle$ is plotted versus relative temperature $\epsilon=(T_c-T)/T_c$, where T_c was taken from the results of high-temperature series expansions.[33] The relative number of "A" atoms in the "B"-rich phase is larger by a factor of more than 2 compared with the two-dimensional system at the same relative temperature, leading to more and larger clusters than observed in previous calculations[12,34] for the two-dimensional system.

The cluster distribution as a function of cluster size in the three-dimensional system[20,35] is plotted in Fig. 3(a) for three different temperatures below T_c. For comparison, the droplet-model predictions Eqs. (6) and (7) for $h\equiv\Delta\mu=0$ are given. The parameters τ, σ, q_0, and q are obtained from the scaling relations Eqs. (11) and (12), together with the values $\delta\approx 5.0$ and $\beta=0.3125$ for the critical exponents, leading to $\tau=2.2$ and $\sigma=0.64$. The different curves (a) and (b) in Fig. 3(a) are due to different evaluations of the amplitudes q_0 and a.

For the coexistence curve we have,[12] from Eq. (7) ($h=0$)

$$\frac{\delta\langle s\rangle}{\partial\epsilon}=\beta\mu_\epsilon\epsilon^{\beta-1}=2q_0a\frac{J}{k_BT_c}\sum_{c=1}^{\infty}l^{1-\tau+\sigma}\exp\left(-a\frac{J}{k_BT_c}\epsilon l^{\sigma}\right), \tag{13}$$

where the sum may be replaced by an integral for $\epsilon\to0$ to give

$$\beta\mu_\epsilon\epsilon^{\beta-1}=\frac{2q_0}{\sigma}\left(a\frac{J}{k_BT_c}\right)^{-[(2-\tau)/\sigma]}\Big/\Gamma\left(\frac{2+\sigma-\tau}{\sigma}\right)\epsilon^{-(2+\sigma-\tau)/\sigma}. \tag{14}$$

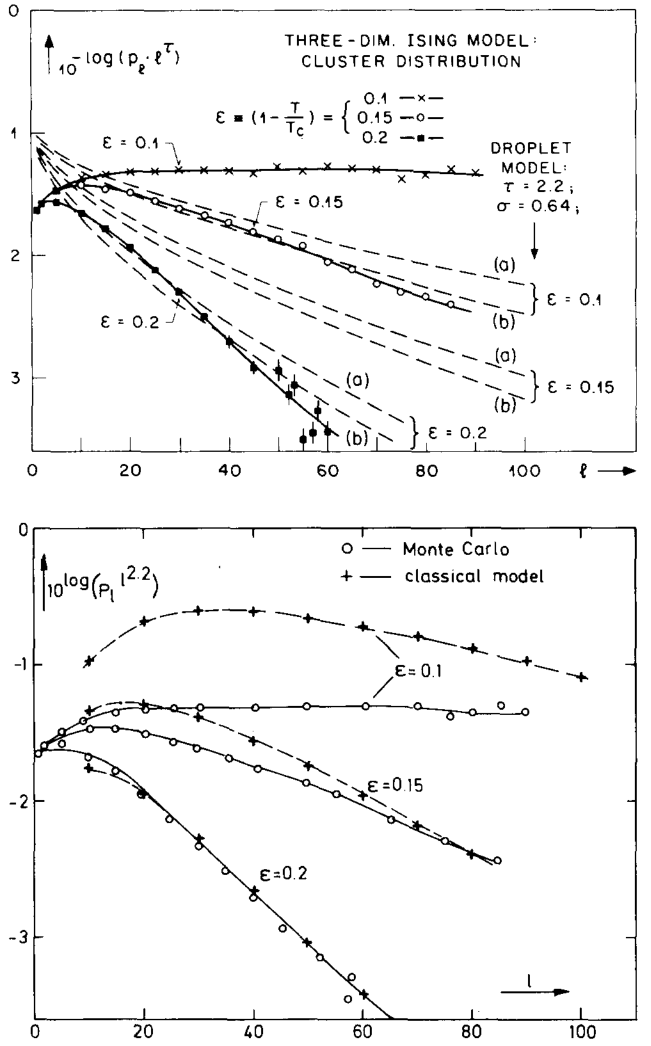

FIG. 3. (a) Cluster distribution in the three-dimensional lattice-gas (Ising) model below T_c at three different relative temperatures $\epsilon \equiv (1-T/T_c)$. The Monte Carlo calculations (full lines) are compared with predictions from scaled droplet model, Eqs. (6) and (7) (broken lines). Approaching T_c there is considerable deviation from the droplet-model predictions. The different curves (a) and (b) correspond to different values for the critical amplitudes (see text). (b) Comparison of the classical droplet model (broken lines) with Monte Carlo data, on the same scales as Fig. 3(a). The classical model was fitted to the data at $\epsilon = 0.2$, $20 < l < 60$. Near T_c, considerable deviation is observed for clusters with $10 < l < 100$. For scaling reasons, however, the classical model cannot be correct for large clusters at $T \to T_c$.

For the critical isotherm, analogously, we have ($\epsilon = 0$)

$$\frac{\partial\langle s\rangle}{\partial h} = \frac{1}{\delta} m_h h^{1/\delta - 1} = \frac{2q_0}{k_B T_c}\left(\frac{h}{k_B T_c}\right)^{\tau-3} \Gamma(3-\tau) , \qquad (15)$$

and from Eqs. (14) and (15) it follows that the amplitudes are $q_0 = 0.105$ and $a = 6.73$ for Curves (a). Curves (b) are obtained in the same way, by choosing, instead of Eq. (15), the relation for the susceptibility[12] (compressibility) to give $q_0 = 0.108$ and $a = 6.26$. An alternative method would be to assume that the cluster distribution Eq. (57) in Ref. 12 holds down to clusters of $l = 1$ particles.[36] This gives, at $T = T_c$,

$$q_0^{-1} = 2\zeta(\tau - 1) , \qquad (16)$$

where ζ is the Riemann ζ function, leading to a smaller value for q_0. The differences in the amplitude "a" result from small uncertainties in amplitudes m_ϵ and m_h in Eqs. (15) and (16) and in the susceptibility. They are significantly smaller than the deviation of the Monte Carlo data from either one of the curves. We also compared the classical droplet formula Eq. (5) with $\sigma = (d-1)/d$ with our data. Since the amplitudes q_0 and a are then not defined by relations like Eqs. (13)–(16), we fitted the data at $\epsilon = 0.2$, giving $q_0 = 0.0029$ and $a = 12.8$ under the simplest assumption, $\tau = 0$. For the range l of the available Monte Carlo data the approximation becomes systematically worse [see Fig. 3(b)] as T approaches T_c. This deviation is still increased as the exponent τ according to Lothe and Pound[37] is assumed to be $\tau = -4$.

Comparing these results with previous Monte Carlo calculations in the two-dimensional system,[34] less agreement is found for the three-dimensional case. In particular, the region of small clusters, where the cluster probability $-{}_{10}\log(p_l l^\tau)$ increases with increasing l, is larger than in the two-dimensional case because of the relatively larger contribution of the surface in the three-dimensional case for $l \approx 10$.

Another difference between the two- and three-dimensional systems becomes important as T approaches T_c.[38] In order to have an order parameter $\langle s\rangle \neq 0$ in an Ising lattice with $\Delta\mu = 0$, an infinitely large cluster of A or B atoms has to exist. Such a cluster, extending in every direction over the whole system, is called a percolating cluster. For a three-dimensional simple cubic lattice[39–42] with noninteracting sites, there is a critical percolation density of ≈ 31% randomly distributed atoms of the same type to form a percolating cluster. This means that both phases (A- or B-type) percolate at the same time, if their relative density is between 31% and 69%. For an Ising system with interaction it was recently shown[38] that this range is even increased so that both phases are percolating simultaneously at relative densities between ≈ 20% and 80%. This interval is reached for $T \gtrsim 0.95 T_c$, i.e., below the critical point. (The two phases of the system percolating each other are then similar to a water-saturated sponge.)

This result indicates that the attractive interaction[38,43–46] between particles of the same type leads to assembling the single clusters onto the largest one, while the interface between this cluster and the surrounding phase remains very diffuse. Such a cluster, of course, will affect the probability distribution of the droplet model close to T_c. For the thermodynamics considered here, the appearance of such a cluster is not necessarily connected with a singularity. Since the cluster is very incompact, it could be broken into pieces by substituting a relatively small number of atoms which connect different regions of the cluster. Similarly, leading to an increasing percolation threshold, we could propose to define clusters in such a way that the only atoms that are counted are those connected and in addition surrounded by the full coordination number of equal particles.

For the two-dimensional system the situation is much simpler. Below T_c, only the phase giving the order parameter can percolate,[39] while the other phase just forms isolated clusters, as is obvious from topological considerations. The critical percolation density in the two-dimensional system[44] is reached at T_c, while above T_c neither component can form a percolating cluster.

If one is below the above-mentioned percolation temperature in the three-dimensional system one may consider the clusters as noninteracting fluctuations (in static approximation). Since the magnetization fulfills the scaling condition as shown in Fig. 2, the cluster distribution p_l must also show a scaling behavior according to the sum rule Eq. (6) together with Eqs. (9) and (10). The Fisher model, Eq. (7), and Reatto's generalization, Eq. (8), predict the scaling variable $\tilde{l}$ to be

$$\tilde{l} \equiv l^{\sigma}\left(\frac{J}{k_B T} - \frac{J}{k_B T_c}\right) . \tag{17a}$$

The cluster distribution p_l can then be written as a homogeneous function in the relative temperature $(J/k_B T)(1 - T/T_c)$ and the cluster size l as

$$p_l^{(T)} = l^{\tau} \tilde{p}(\tilde{l}) . \tag{17b}$$

As is already clear from Fig. 3(a), this is not a good choice in the three-dimensional system, although it gave good agreement with scaling theory in the two-dimensional system below T_c. As long as the cluster size l is the most relevant parameter for the properties of a single cluster (in comparison with, for example, the possibly different shapes of clusters of the same size) the scaling form Eq. (17) should hold. Near the percolation threshold, however, several relatively compact clusters may be connected by thin bridges consisting of relatively few particles forming a giant but relatively diffuse cluster. Small changes in shape of these connected clusters may break them apart, leaving several smaller clusters instead of a large one at the cost of very few broken bonds. In this case, therefore, one should expect a formula for the cluster statistics also to consider fluctuations in the cluster shape. This additional degree of freedom may formally be taken into account by additional critical exponents, if we write the cluster probability in the form of a generalized homogeneous function

$$p(l,s) = l^{-\tau_B} \tilde{p}(\epsilon l^{z}, h l^{y}, s l^{-x}) , \tag{18}$$

where l is the cluster size, s is the number of nearest-neighbor bonds between the cluster and the surrounding phase, and $\{\tau_0, z, y, x\}$ are the critical exponents which may be related to those of the macroscopic thermodynamic quantities.

This scaling form is based on the assumption that the next relevant variable is the cluster surface s. From the scaling relations for the internal energy of the system $U \sim s$, one then obtains expressions for the present exponents in terms of the original exponents α, β, γ, δ, etc. These relations were recently derived by Binder.[47]

With the help of Eq. (6) and replacing the sum by an integral analogous to the procedure used around Eqs. (13)–(15), one obtains from Eq. (18) for the coexistence line ($h = 0$)

$$\frac{\partial\langle s\rangle}{\partial h} \sim \epsilon^{-(2-\tau+y)/z} \rightarrow \gamma = \frac{2-\tau+y}{z} , \tag{19}$$

for the critical isotherm ($\epsilon = 0$)

$$\frac{\partial\langle s\rangle}{\partial h} \sim h^{-(2-\tau+y)/y} \rightarrow \beta\delta = y/z , \tag{20}$$

and for the specific heat at the coexistence line

$$\frac{\partial u}{\partial \epsilon} \sim \epsilon^{-\alpha} \rightarrow \alpha = \frac{1-\tau+z+x}{z} . \tag{21}$$

Since the cross derivatives of the free energy are symmetric,

$$\frac{\partial^2 G}{\partial\epsilon\,\partial h} = \frac{\partial^2 G}{\partial h\,\partial\epsilon} , \tag{22}$$

one has

$$\frac{\partial u}{\partial h} \sim \frac{\partial\langle s\rangle}{\partial\epsilon} \sim \epsilon^{\beta-1} \rightarrow \beta - 1 = \frac{1-\tau+y+z}{z} . \tag{23}$$

This implies that the scaling relation $2 - \alpha = \beta(\delta + 1)$ holds and x can now be related to the exponents y and z,

$$x = z - y + 1 = 1 - z(\beta\delta - 1) . \tag{24}$$

For the present investigation we shall not consider the coordinate s explicitly, i.e., we shall not make an assumption what the next relevant variable in addition to the cluster size should be, but we shall only discuss a possible scaling form,

$$p_l = l^{-\tau_0} \tilde{p}(\epsilon l^{z}, h l^{y}) , \tag{25}$$

where the restriction $y = 1$ of previous cluster distribution formulas Eqs. (7) and (8) is no longer maintained.

Involving again the scaling relations Eqs. (9)–(11) together with the sum rule Eq. (6), we can write more explicitly

$$p_l = l^{-(2+y/\delta)} \tilde{p}(\epsilon l^{y/\beta\delta}, h l^{y}) . \tag{26}$$

This is also obtained from previous scaling forms Eqs. (7) and (8) by replacing the coordinate l by a generalized cluster-size coordinate $l' = l^{y}$, requiring that Eq. (6) be fulfilled. For convergence reasons y has to be within the limits $0 < y < \beta\delta/[d(\beta\delta - 1)]$.

The physical meaning of this generalized coordinate can be understood in the following way. Close to T_c, local deviations in the concentration from the expectation value $\langle s\rangle$ have a characteristic linear extension of the order of the correlation length $\xi \sim \epsilon^{-\nu}$. In the cluster picture given above, these fluctuations correspond to the "relatively compact" parts of a cluster, which are connected by thin bridges of relatively few particles.

The total number l of particles in the cluster therefore must be at least of the order $l \gtrsim \xi^{d}$. Since the size of a typical cluster contributing to the singular part of the free energy is $\epsilon l^{y/\beta\delta} = \text{const}$—according to Eq. (26) in the concept of scaling theory—one has a restriction for the new exponent y:

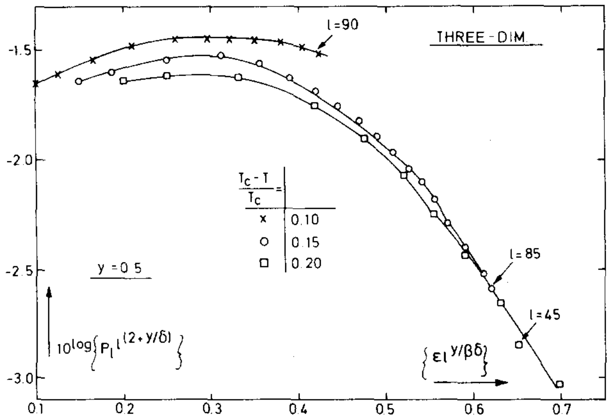

FIG. 4. Scaled cluster concentration $_{10}\log(p_l l^{(2+y/\delta)})$ in three dimensions plotted versus the scaled cluster-size variable $\tilde{l} = \epsilon l^{y/\beta\delta}$, involving a new exponent y. For the two lower temperatures $\epsilon = \{0.15, 0.2\}$, the cluster probabilities scale with $y = 0.5$, while for $\epsilon = 0.1$, the statistics are no longer good enough to decide whether scaling can be achieved.

$$y \leq (1 + 1/\delta)^{-1} . \tag{27}$$

This inequality takes into account that clusters in general are not necessarily "compact" structures but may consist of diffuse agglomerations of relatively compact regions. The coordinate $l' = l^y$ then describes the total excess concentration produced by a cluster of l particles; the associated free energy is accordingly the excess free energy of a cluster.

We have tried to find best fits of the scaling formula Eq. (26) to the Monte Carlo data at the three temperatures $\epsilon = 0.2$, 0.15, 0.1. As plotted in Fig. 4, the cluster statistics for the two lower temperatures scale rather well with an exponent $y = 0.5$, while the data for $\epsilon = 0.1$ closest to T_c are somewhat inconclusive owing to the limited cluster size $l \lesssim 100$. Comparing this value of y with the original Fisher model[19] $y = 1$ [Eq. (7)], one finds a remarkable deviation. This indicates that agglomeration of "compact" clusters to larger cluster networks takes place as T_c is approached, in agreement with the observation of percolating (infinite) clusters close to the critical point. In the immediate neighborhood of T_c the extent of a cluster, which is defined as particles connected by nearest-neighbor bonds, is therefore no longer a direct measure of the correlation length. A formal relation between these two quantities was given here, introducing the generalized cluster coordinate $l' = l^y$. The value of this exponent y depends then upon other degrees of freedom for the clusters such as total surface and shape. Verification of these details would require additional computer simulations which use an exorbitant amount of computer time for three-dimensional systems.

In the following instead we investigate the scaling behavior of the two-dimensional Ising model above the percolation temperature, which coincides in that case with the critical point.[44,48]

IV. TWO-DIMENSIONAL SYSTEM ABOVE T_c

The usual cluster models such as Eqs. (4), (5), and (7) are clearly constructed for the two-phase region, where the component of relatively lower concentration is described by the cluster concept, while the component of relatively higher concentration is taken as surrounding medium. Above T_c this natural bias of course no longer exists. The usual cluster formulas Eqs. (5) and (7) clearly cannot hold in the case of zero field (chemical potential difference) $\Delta\mu = 0$, since the surface free-energy term $A(T)$ changes sign at T_c. The multiplicative correction suggested by Reatto[23] [Eq. (8)] was assumed to account for the noncompactness of clusters near and above T_c, since only the compact clusters were assumed to contribute to the singular part of the free energy. For scaling reasons the two variables, relative temperature ϵ and cluster coordinate l, have to occur in the same combination as in the exponential Eq. (5). But as we have seen in the three-dimensional case the cluster distribution p_l does not scale in that simple form of Eq. (7) or Eq. (8) but requires a more severe modification such as, for example, Eq. (25).

In the two-dimensional system below T_c, the simple Fisher model Eq. (7) [or more general Eq. (25) with $y = 1$] gave very satisfactory agreement with Monte Carlo data. Our present investigations on a 110×110 site lattice above T_c also support the scaling behavior as plotted in Figs. 5(a) and (b). In Fig. 5(a) the unscaled plot for three temperatures above T_c is given in the same way as in Fig. 3. The remarkable difference is the continuing increase with l of the renormalized clus-

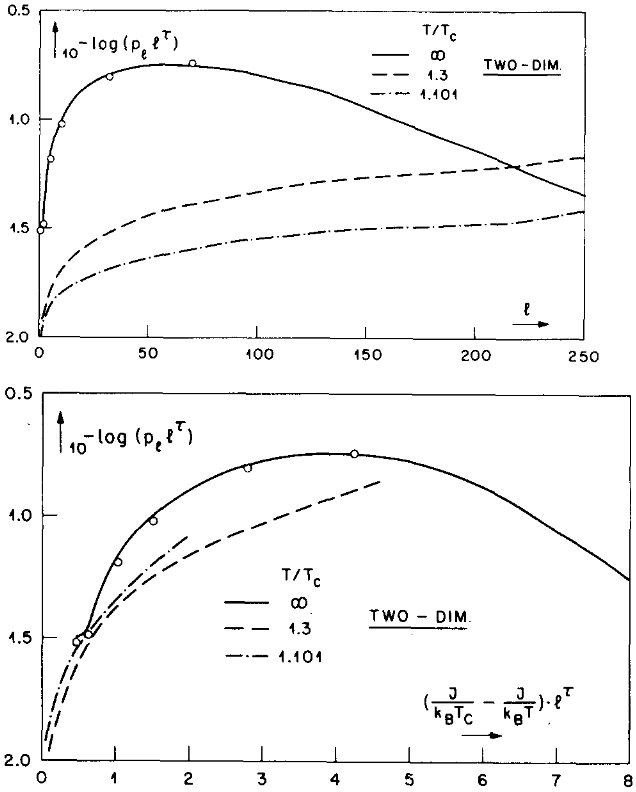

FIG. 5. (a) Cluster distribution in two dimensions above T_c, for three temperatures as obtained from Monte Carlo calculations. Circles denote the data of Dean and Bird at infinite temperatures (Ref. 41). (b) The same data as in Fig. 5(a), but now plotted versus the scaled variable [Eq. (17a)]. (Erratum: the exponent should be σ instead of τ.) Near T_c ($T \leq 1.3\ T_c$) the data scale up to a cluster size of $l \approx 500$.

ter distribution $-{}_{10}\log(p_l l^\tau)$, indicating that one is not yet in the asymptotic region of exponential decay [according to Eqs. (5) and (9)]. More precisely: while l is large, the scaled $\tilde{l}$ of Eq. (17a) is still of order unity. Contrary to the simpler ferromagnetic side, therefore, one does not have[49] a simple exponential law like $\exp(-a\tilde{l})$ for all scaled $\tilde{l}$ but at best for large $\tilde{l}$, and this latter asymptotic region has not yet been reached closely above T_c. In Fig. 5(b) the same data are plotted, but now versus the scaled variable Eq. (17a). The data at $T/T_c = 1.101$ and 1.3 fall almost onto the same curve up to a cluster size of $l \approx 500$. The deviations for larger clusters may be due to statistical errors caused by long-time memory effects of these large clusters, even though the total computing time was rather long: 2500 MC steps/site at $T=\infty$, 30 000 steps at $T/T_c = 1.3$, and 40 000 at $T/T_c = 1.101$. We have compared the cluster formula of Reatto,[23,24]

$$p_l l^\tau = q_0 \frac{\exp(-a\tilde{l})}{[B\exp(-ba\tilde{l})+1]} \quad \tilde{l} \text{ from Eq. (17a)}, \qquad (28)$$

with the data on Fig. 5(b). A least-squares fit to the two curves suggests $q_0 \approx 0.06$, $a \approx 0.1$, $B \approx 3$, and $b \approx -8$. These values are completely incompatible with values $q_0 \approx 0.02$, $a \approx 5$ obtained from fitting Eqs. (5) and (7) to the MC data below T_c, or with values $b \approx 2.5$, $B \approx 0.05$ of Reatto and Rastelli's[24] comparison with series-expansion results. In fact, the negative sign of $b < 0$ would lead to a divergence of Eq. (28) for large $l \to \infty$. It is clear that the probability p_l must asymptotically ($l \to \infty$) decrease exponentially at any finite temperature $T \neq T_c$. The Monte Carlo data up to $l \lesssim 2000$ are clearly not yet in this asymptotic region. Although they exhibit scaling behavior, they cannot be fitted by a reasonable set of the parameters entering Eq. (28). We therefore conclude that neither can this formula describe the statistics of nearest-neighbor-bond clusters above T_c. In fact, the formula seems to be much more appropriate to describe cluster statistics around the percolation threshold[49] since the latter transition explicitly relies on the geometric definition of clusters.

For infinite temperatures $T=\infty$, scaling theory is obviously no longer expected to hold, since the system is equivalent to a random distribution of interaction-free particles at arbitrary temperature. This case[21,39–43,48–53] is now of particular interest for the theories of percolation and of dilute (magnetic) systems. Early simulations were already carried out ten years ago by Dean and Bird[41] (data are plotted in Figs. 5 and 6). Unfortunately, they gave only cumulative data for cluster sizes $l > 10$, namely, sums over p_l for $l = 11$–20, 21–50, 51–100, 101–1000, 1001–10 000. We therefore used our data, which have better statistics by a factor of 25 than in Ref. 41, to check on recent theories of dilute magnets. Above T_c neither component in the two-dimensional two-component system can percolate, at $T=\infty$ the ("site") percolation density is $\approx 59\%$ for one component, while in our case for $\Delta\mu/k_B T = 0$ we have 50% for both, thus being below the percolation threshold.

Griffiths[51] showed that the equation of state $M(q, H, T)$ for a randomly dilute ferromagnet cannot be analytic, where q is the fraction of lattice sites occupied by spin variables $\sigma_i = \pm 1$, H is the magnetic field, T is the temperature, and M is the magnetization. In our lattice gas model these sites with $\sigma_1 = \pm 1$ would correspond to the sites occupied by atoms; in the terminology of an A–B binary mixture they would correspond to the sites occupied by, for example, A atoms, while the empty spaces are characterized by the B atoms. (The additional degree of freedom of the spin variables $\sigma_i = \pm 1$ is not of importance in this context.) Domb,[54] Brooks, and Harris[50] and Bakri and Stauffer[21] discussed the nature of this nonanalyticity for $H \to 0$, which is very probably an essential one. The magnetization in a field can be represented by a sum over the clusters

$$M \sim \sum_{l=1}^{\infty} l p_l \tanh\left(\frac{lH}{2k_B T}\right), \qquad (29)$$

where the temperature is assumed to be so low that all spin variables within one cluster have equal sign. It is now argued that the probability for these clusters asymptotically [see Eq. (28)] behaves as

$$p_l \sim \exp[-\text{const}(l^\zeta)] \quad \zeta > 0. \qquad (30)$$

For the Bethe lattice[50] it was shown that $\zeta = 1$ both for $q < q_c$ and $q > q_c$. For real lattices, Bakri and Stauffer argue that $\zeta \approx 0.4$ for $q > q_c$ but again give $\zeta = 1$ for $q < q_c$, while Reatto[24] suggested $\zeta = 1/(\beta+\gamma) < 1$ both for $q \gtrless q_c$. Our Monte Carlo calculations at zero interaction energy (or infinite temperature) can provide information on the behavior for $q < q_c$.

At $T=\infty$ we are far away from the Curie temperature. But a scaling hypothesis has been proposed also for the percolation transition at $q = q_c$, based on a variant of Fisher's droplet model.[49] Right at $q = q_c$ one expects a decay of the cluster-size distribution as $p_l \sim l^{-\tau}$. For percolation, the critical exponents like τ, β, etc. are different from the Ising model at the Curie temperature[55] and also the exponents η (and thus Δ) are no exceptions.[52] However, for $d=2$ one has[56,57] δ near 18 and thus τ is very close to its value at the Curie temperature.

For two dimensions, therefore, we can take the same τ as before even at $T=\infty$ without introducing noticeable errors. Monte Carlo data as plotted in Fig. 5 ($T=\infty$) first show an increase in the renormalized cluster statistics, and above $l \gtrsim 60$ the exponential decay takes over. Equation (30) is expected to hold asymptotically only. We therefore drop the initial data with $l < 60$ by renormalizing all data with respect to the maximum of $-{}_{10}\log(p_l l^\tau)$ at $l \approx 60$. This leads to

$$\frac{p_l l^\tau}{(p_l l^\tau)_{\max}} \sim e^{-\text{const}(l-l_{\max})^\zeta}, \quad l_{\max} = 60, \qquad (31)$$

which is asymptotically completely equivalent to Eq. (30), or alternatively,

$$\ln\left|\ln \frac{p_l l^\tau}{(p_l l^\tau)_{\max}}\right| \sim \zeta \ln(l - l_{\max}) + \text{const}. \qquad (32)$$

Plotting the data in the variables of Eq. (32) we expect asymptotically a straight line with slope ζ. This can be seen in Fig. 6, where we do indeed find a slope of ζ

$= 1.1 \pm 0.1$ up to our largest clusters counted with $l \approx 800$. This confirms the analyses of Refs. 21 and 50 predicting a simple exponential decay [Eq. (30)] of the cluster probability in a random dilute ferromagnet below the percolation density. On the other hand, the strong maximum in $p_l l^\tau$ as a function of l is also seen, as predicted first by Reatto,[23] proving that the paramagnetic cluster-size distribution (in the percolation problem) is not a simple exponential, in contrast to the simpler ferromagnetic case.

We finally show in Fig. 7 a fit of the extended cluster distribution formulas given by Stauffer,[58]

$$p_l l^\tau = p_0 \exp(+Al + Bl^\sigma) \, , \tag{33}$$

using the percolation exponents $\sigma \approx 0.39$, $\tau \approx 2.056$. The parameters p_0, A_1, and B were fitted. We find remarkable agreement over the whole range of cluster sizes between $50 \le l \le 750$, the behavior for large l being dominated by the linear behavior as seen in Fig. 6.

V. CONCLUSION

We have investigated cluster statistics on lattice systems which allow for an unambiguous definition of clusters. They are defined as sets of particles which are connected by at least one-nearest-neighbor bond.

Of particular interest—with respect to thermodynamic properties of the system—is the neighborhood of the critical temperature. In the three-dimensional system the cluster statistics are very much influenced by the appearance of a percolating cluster even slightly below T_c.[38] The expected scaling behavior therefore is not observed for these clusters, but presumably holds only for the relatively compact parts of these "sponge"-like clusters. Formally, one may account for these deviations from a "compact" shape by a transformation of the cluster-size variable l to $l' = l^y$ with an additional critical exponent y. In Fisher's droplet model[19] and several modifications,[23-26] the value is implicitly assumed to be $y = 1$. For the three-dimensional model at 10% below T_c, a value of $y = 0.5$ gives a considerably better fit to the data.

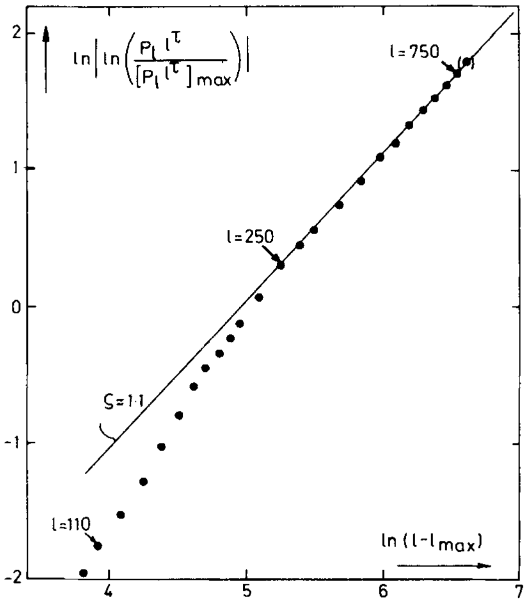

FIG. 6. Asymptotic behavior ($l > l_{max}$, see text) of the cluster distribution in a two-dimensional system of noninteracting particles below the percolation threshold. The slope $\zeta = 1.1 \pm 0.1$ confirms previous predictions (Refs. 21 and 50) on a simple exponential decay of the cluster probabilities in a randomly dilute ferromagnet.

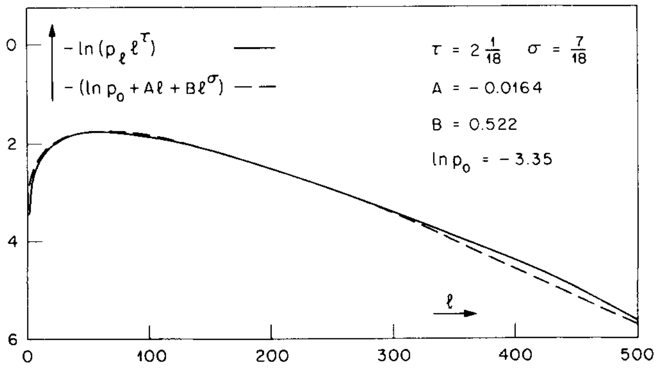

FIG. 7. Cluster distribution as in Fig. 6, but fitted to the formula Eq. (33) (Ref. 58). For the fitted parameters $\ln p_0 = -3.35$, $A = -0.0164$, $B = 0.522$, we obtained very good agreement over the whole range of cluster sizes $50 \le l \le 500$.

Since percolation is present in the whole range of $T > T_c$ for the three-dimensional system, we investigated instead a two-dimensional system to check predictions of cluster-probability formulas above T_c. We found that the cluster distributions for $T > T_c$ can be represented essentially by a single curve, which supports the scaling assumptions in a similar way as obtained below T_c in two dimensions. On the other hand, no agreement with explicit cluster-distribution formulas was found above T_c. Fitting Reatto's[23,24] formulas led to inconsistencies with the values for $T < T_c$. This might be due to the fact that our statistics may not yet be in the asymptotic regime of sufficiently large clusters. But since the largest clusters counted (up to $l \approx 2000$) are already of macroscopic size, the range of applicability of these cluster formulas above T_c at best appears to be rather limited.

For $T \to \infty$ or, equivalent, for vanishing interaction energy between particles, we could show that the probability for clusters in a dilute system (below the percolation threshold) decays asymptotically $\sim \exp(-\text{const}\, l^\zeta)$ with $\zeta \approx 1$. This confirms the previous analysis[21] of Dean and Bird's[41] data. Accordingly, the existence of an essential singularity[51] at zero magnetic field in the equation of state for randomly dilute low-temperature ferromagnets is supported, following the arguments of Bakri and Stauffer.[21]

ACKNOWLEDGMENT

We are indebted to D. Stauffer for his continuing interest and his detailed comments, and thank K. Binder and C. Domb for discussions.

---

*This work was carried out while at the IBM Zurich Research Laboratory.

†Temporary address until June 1977: Physics Dept., Carnegie-

Mellon University, Pittsburgh, PA.

[1] M. Volmer and A. Weber, Z. Phys. Chem. **119**, 277 (1926).

[2] R. Becker and W. Döring, Ann. Phys. 24, 719 (1935).

[3] J. Mayer, J. Chem. Phys. 5, 67 (1937).

[4] J. Feder, K. Russel, J. Lothe, and M. Pound, Adv. Phys. 15, 117 (1966).

[5] I. Lifshitz and V. V. Slyozov, J. Phys. Chem. Solids 19, 35 (1961).

[6] B. Chakraverty, in *Crystal Growth*, edited by P. Hartmann (North-Holland, Amsterdam, 1973), p. 50.

[7] K. Binder and D. Stauffer, Phys. Rev. Lett. 33, 1006 (1974).

[8] J. Cahn and J. Hilliard, J. Chem. Phys. 28, 258 (1958).

[9] J. Langer and L. Turski, Phys. Rev. A 8, 3230 (1973).

[10] K. Sarkies and N. Frankel, Phys. Rev. A 11, 1724 (1975).

[11] T. Schneider and E. Stoll, in *Anharmoic Lattices, Structural Transitions and Melting*, edited by T. Riste (Nordhoff, Leiden 1974), p. 275.

[12] K. Binder and H. Müller-Krumbhaar, Phys. Rev. B 9, 2328 (1974).

[13] For a review, see *Nucleation*, edited by A. Zettlemoyer (Marcel Dekker, New York, 1969); *Nucleation II* (Marcel Dekker, New York, to be published).

[14] D. Stauffer, G. Walker, G. Brown, J. Wise Jr., and C. Kiang, J. Aerosol Sci. 5, 157 (1974).

[15] J. K. Lee, J. A. Barker, and F. F. Abraham, J. Chem. Phys. 58, 3166 (1973).

[16] For reviews, see M. E. Fisher, Rep. Prog. Phys. 30, 615 (1967), and C. Domb, *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. Green (Academic, New York, 1972), Vol. 3, p. 357.

[17] J. M. Levelt-Sengers and J. V. Sengers, Phys. Rev. A 12, 2622 (1975) and references therein; R. Hocken and M. Moldover, Phys. Rev. Lett. 37, 29 (1976).

[18] L. Landau and E. Lifshitz, *Statistische Physik* (Akademie, Berlin, 1970).

[19] M. E. Fisher, Physics 3, 255 (1967).

[20] H. Müller-Krumbhaar, Phys. Lett. A 48, 459 (1974).

[21] M. M. Bakri and D. Stauffer, Phys. Rev. B (to be published).

[22] A. Martin-Löf, Commun. Math. Phys. 32, 75 (1973); see also A. Andrev, Zh. Eksp. Teor. Fiz. 45, 2064 (1963).

[23] L. Reatto, Phys. Lett. A 33, 519 (1970).

[24] L. Reatto and E. Rastelli, J. Phys. C 5, 2785 (1972).

[25] C. S. Kiang and D. Stauffer, Z. Phys. 235, 130 (1970).

[26] D. Stauffer, C. Kiang, G. Walker, O. Puri, J. Wise, and E. Patterson, Phys. Lett. A 35, 172 (1971).

[27] H. Stanley, *Phase Transitions and Critical Phenomena* (Clarendon, Oxford, 1971).

[28] K. Kinder, D. Stauffer, and H. Müller-Krumbhaar, Phys. Rev. B 12, 5261 (1975); *ibid.* 10, 3853 (1974).

[29] K. Binder and D. Stauffer, J. Stat. Phys. 6, 49 (1972).

[30] K. Binder and D. Stauffer, Adv. Phys. 25, 343 (1976).

[31] H. Müller-Krumbhaar and K. Binder, J. Stat. Phys. 8, 1 (1973).

[32] H. Müller-Krumbhaar (unpublished).

[33] D. S. Gaunt and C. Domb, J. Phys. C 3, 1442 (1970); J. W. Essam and D. L. Hunter, J. Phys. C 1, 392 (1968); D. S. Gaunt, Proc. Phys. Soc. London 92, 150 (1967).

[34] E. Stoll, K. Binder, and T. Schneider, Phys. Rev. B 6, 2777 (1972).

[35] Some preliminary results were also given in Ref. 20.

[36] C. S. Kiang, Phys. Rev. Lett. 24, 47 (1970).

[37] J. Lothe and G. Pound, J. Chem. Phys. 36, 2080 (1962).

[38] H. Müller-Krumbhaar, Phys. Lett. A 50, 27 (1974).

[39] J. W. Essam, *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. Green (Academic, London, 1973), Vol. 2, p. 197.

[40] S. Kirkpatrick, Rev. Mod. Phys. 45, 574 (1973).

[41] P. Dean and N. F. Bird, National Laboratory, Teddington, England, Report No. MA 61, 1966.

[42] Further computer-simulation data are due to G. Quinn, G. Bishop, and R. Harrison, J. Phys. A 9, L9 (1976); K. Duff and V. Canella, *Amorphous Magnetism*, edited by H. Hooper and A. de Graaf (Plenum, London, 1973), p. 207; C. Domb, T. Schneider, and E. Stoll, J. Phys. A 8, L90 (1975); K. Onizuka, J. Phys. Soc. Jpn. 39, 527 (1975); M. Levinshtein, B. Shklovskij, M. Shur, and A. Efros, Zh. Eksp, Teor. Fiz. 69, 386, 2203 (1975); P. L. Leath, Phys. Rev. Lett. 36, 921 (1976); A. Sur, E. L. Lebowitz, J. Marro, M. H. Kalos, and S. Kirkpatrick, J. Stat. Phys. (to be published).

[43] R. Kikuchi, J. Chem. Phys. 53, 2713 (1970).

[44] T. Odagaki, N. Ogita, and H. Matsuda, J. Phys. Soc. Jpn. 39, 618 (1975).

[45] T. Odagki, Progr. Theor. Phys. (Kyoto) 54, 1067 (1975).

[46] A. Coniglio, Phys. Rev. B 13, 2194 (1976).

[47] K. Binder, Ann. Phys. (New York) 98, 390 (1976).

[48] R. Griffiths and L. Lebowitz, J. Math. Phys. 9, 1284 (1968).

[49] D. Stauffer, Phys. Rev. Lett. 35, 394 (1975).

[50] A. Brooks Harris, Phys. Rev. B 12, 203 (1975).

[51] R. Griffiths, Phys. Rev. Lett. 23, 17 (1968).

[52] A. B. Harris, T. O. Lubensky, W. Holcomb, and C. Dasgupta, Phys. Rev. Lett. 35, 327 (1975).

[53] A. Young and R. Stinchcombe, J. Phys. C 8, L 535 (1975).

[54] C. Domb, J. Phys. A 9, 283 (1976).

[55] S. Kirkpatrick, Phys. Rev. Lett. 36, 69 (1976).

[56] M. F. Sykes, D. S. Gaunt, and M. Glen, J. Phys. A 9, 97 (1976).

[57] D. S. Gaunt and M. F. Sykes, J. Phys. A 9, 1109 (1976).

[58] D. Stauffer, J. Phys. C 8, L172 (1975).