

MODIFIED FISHER DROPLET MODEL

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ABSTRACT

We propose a simple modification of the Fisher droplet model which, unlike classical nucleation theory, reproduces very well some Monte Carlo equilibrium cluster distributions p_1 for the three-dimensional Ising or lattice gas model. It then follows that $p_1(h)/p_1(h=0) = A \exp(-\eta l)$ where $\eta \propto h^{1/y}$, $y \approx 0.45$, when the magnetic field h is small enough, as suggested from the consideration of an effective cluster size l^y , while η seems rather proportional to h at larger values of the field, as implied by some exact results.

INTRODUCTION

A simple cubic lattice of N vertices or sites with periodic boundary conditions, each site having two states, "occupied by a particle" and "unoccupied", with a constant attractive interaction V between nearest-neighbor particles, is a familiar realization of the lattice gas model [1,2]. The relevant (configurational) energy of the system in the configuration C is defined as

$$E(C) = -V \sum_{(i,j)} n_i n_j, \quad V > 0. \quad (1)$$

Here n_i is the occupation number of the i th site which, for a given configuration C , takes on the value 1 if site i is occupied and the value 0 if site i is unoccupied, C denotes the subset of the lattice comprising the $\sum_i n_i$ occupied sites, $\sum_{(i,j)} n_i n_j$, and the sum goes over all pairs (i,j) of different sites, each pair being counted once only, which are nearest-neighbors in the lattice.

There are a total of 2^N possible configurations on the lattice. In a grand canonical ensemble at temperature T and fugacity z the probability of the configuration C is

$$p(C) = z^{\sum_i n_i} \exp[-E(C)/kT] \Xi(z, T; N)^{-1} \quad (2)$$

where $\Xi = \sum_C z^{\sum_i n_i} \exp(-E/kT)$ is the grand partition function [2]. Any configuration C can be partitioned into subsets C_r called clusters defined as sets of occupied sites connected by bonds. A bond is a pair of nearest-neighbor sites in the lattice. The size l_r of a given cluster C_r is defined as the number of (occupied) sites which belong to C_r ; its energy s_r is defined as the number of occupied-unoccupied bonds (including both, surface and interior ones) incident on C_r . The average degree of compactness of clusters may be measured, at least partially, in terms of s_1 , the average value of s_r over all clusters of size 1. This information is to be combined with the knowledge of p_1 , the probability for the occurrence of a cluster of size 1 in the system, which is induced by the Gibbs probabilities (2).

The description of the system configuration at temperature T and density ρ in terms of clusters via the quantities s_1 and p_1 has both

physical and mathematical interest in the percolation problem, in the theory of metastable states and nucleation processes in a lattice gas or Ising spin system and in many other problems [3-6]. The physical relevance of the concept of clusters comes in part from the fact that they are expected to be related in some cases to the grains or droplets observed by transmission electron microscopy. Different assumptions and models concerning s_1 and p_1 are nowadays controversial, however, and it is even unclear what should be the most useful and precise definition for a cluster [6-8]. It is the purpose of this paper to discuss and extend some ideas concerning s_1 and p_1 in the case of the nearest-neighbor lattice model described before and to relate them to Monte Carlo data along the coexistence line and close to it in the one phase region [8].

CLUSTER DISTRIBUTION

The above definition for a cluster implies that two different clusters cannot overlap. Moreover, no sites in different clusters can be nearest-neighbors so that one has from Eq. (1) that $E(C) = \sum_r E(C_r)$. This means in practice that we may regard our clusters as independent systems [9].

Let B_r denote the border sites of cluster C_r , i.e. the set of (unoccupied) sites not in C_r that are nearest-neighbors of sites in C_r . The probability for the occurrence of C_r , $p(C_r)$, can then be written as the conditional probability that all sites of C_r are occupied, given that all sites of B_r are unoccupied, times the probability that all sites of B_r are unoccupied. The problem here is to conclude an explicit expression for p_1 .

The Fisher droplet model [5] gives, along the coexistence line,

$$p_1 = p_0 l^{-\tau} \exp[-a(T) l^{\sigma}] \quad (3)$$

where $a(T) = a_0 (T_c/T - 1)$. This is based on the assumptions that p_1 is proportional to $\exp(-e_1/kT)$, that the energy e_1 of an l -cluster has a predominant contribution from its surface, and that this behaves like l^{σ} . The "entropical" factor $l^{-\tau}$ in Eq. (3) takes into account the number of clusters of size l with different shapes. This is expected to be irrelevant for large enough l and nucleation theories [4] usually set $\tau = 0$ and $\sigma = 2/3$; while the value $\sigma = 2/3$ is suggested from some exact results at $l \rightarrow \infty$ [12], $\tau \neq 0$ or some other non-dominant l -correction seems important in order to describe Monte Carlo data where one observes small (say, $l \leq 10$) as well as "large" (say, $100 \leq l \leq 300$) clusters [8]. The term $l^{-\tau}$, $\tau \neq 0$, seems also very important when trying to fit exact values [9] for p_1 at $T \leq 0.5 T_c$ where p_1 becomes quite negligible for, say $l > 10$ [8].

Assuming the validity of Eq. (3) near the critical temperature T_c it readily follows [4-6] $\sigma = 0.64$ and $\tau = 2.2$. The resulting picture with $p_0(T)$ and $a(T)$ adjustable parameters, combined with the sum rule

$$\sum_{l=1}^{\infty} l \cdot p_l = \xi, \quad (4)$$

is known to be inadequate to describe the data [4]. Thus it seems that the only way to maintain an equation like (3) is to allow for a temperature dependence on the exponent τ . One obtains then [8] that $\tau < 0$ for $T < 0.39 T_c$ and $\tau > 0$ increasing monotonically with temperature; e.g. $\tau(0.3 T_c) = -0.78$, $\tau(0.5 T_c) = 0.64$, $\tau(0.8 T_c) = 1.4$, $\tau(0.9 T_c) = 1.65$. This temperature dependence on τ , however, is unpleasant for several reasons. In the first place, because τ was intended to be positive defined and temperature independent [5,13]. Secondly, because the values for $a(T)$ in this case do not follow the requirement [5] that $a(T) \propto (T_c/T - 1)$ (they

even seem to follow the opposite trend [8]). The known values for τ neither seem to give the expected limit $\tau \rightarrow 2.2$ or so as $T \rightarrow T_c$ (see before). Finally, one may obtain a better and more consistent description of the data over a wide range of temperatures and densities with a reasonable modification of the formula (3) which contains in practice less adjustable parameters than Eq. (3) itself.

We propose the modification

$$p_1 = p_0 l^{-\tau} \exp(-a l^{2/3}) [1 - \alpha \exp(-a l^{2/3})] \quad (5)$$

where $a = a(T)$, p_0 is determined by the sum rule (4), and τ and α are temperature (and density) independent. The last factor in Eq. (5) aims to represent approximately the probability of unoccupied sites surrounding the "average cluster" C_1 (i.e., the probability that B_1 is empty) while the Fisher factor is kept to represent the occupation of the set C_1 . We also make the assumption that Eq. (5) should be consistent near T_c with the scaling behavior

$$p_1 = 1 - (2+y/\delta) f(\epsilon l^{y/\rho\delta}) \quad (6)$$

where $\epsilon = (T_c - T)/T_c$ and y is a new critical exponent introducing a cluster effective size l^y [6]. The combination of Eqs. (5) and (6) leads to $\tau = 2 + y/\delta$ and $a(T) = a_0 \epsilon^t$ with $t = 2\rho\delta/3y$; thus it follows that the cluster distribution is determined by the usual critical exponents β and δ and by the constants a_0 , p_0 and y which are to be determined consistently with the sum rule (4) (i.e., no temperature-dependent parameter is left in Eq. (5)).

COMPARISON WITH MONTE CARLO DATA

The above distribution may be tested against some recent Monte Carlo data [8] concerning equilibrium configurations C of the model described before with $N = 125,000$ sites. The data was generated by the familiar method of "quenching" the model system from infinite temperature and letting it to relax toward equilibrium at the coexistence line or in the one phase region. The model system was then allowed to evolve at equilibrium during a large enough time interval to obtain good statistics when performing a time averaging. The details of the computer simulations can be found elsewhere [8,10].

The basic step during the computer simulation is the move of a particle to a neighboring empty site according to a prescribed transition probability satisfying detailed balance [10]. This ensures that ρ remains strictly constant in time, while the system is in contact with a heat bath at temperature T , so that the situation can be described by means of a canonical ensemble. In the thermodynamic limit, $N \rightarrow \infty$, there should be no distinction between our results and those corresponding to the grand canonical ensemble (2). This statement is known to hold already for most practical purposes when $N = 1.25 \times 10^5$ [11] which is the case considered here. One should only warn that "large" clusters for finite N will be different from what they are in the thermodynamic limit. Hence great caution must be exercised in deducing asymptotic, $l \rightarrow \infty$, formulas for s_1 or p_1 from the data, specially when ρ is very small. We are somewhat confident on the data we are dealing with, however, in the sense that it becomes practically indistinguishable [8] when compared with data corresponding to another simulation with $N = 0.5 \times 10^7$, $\rho > 0.015$ [7].

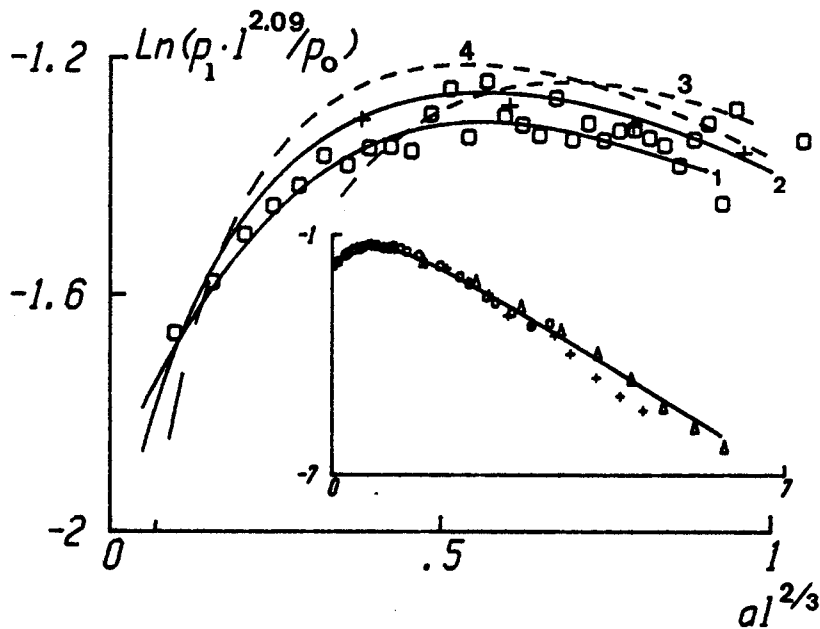


FIG. 1. Eq. (5) with $\zeta = 2.09$, as implied by scaling, adjusts the data (see the inset) corresponding to $T = 0.59 T_c$ (triangles), $T = 0.78 T_c$ (crosses) and $T = 0.89 T_c$ (circles) along the coexistence line when $\alpha = 0.88$, independent of temperature, and $a = a_0 \epsilon^t$, $t = 2 \beta \bar{\delta} / 3\gamma$, as expected. The main figure shows the details around the origin where the differences between different predictions are more significant. Line 1 corresponds to our best description, Eq. (9). Line 2 is the prediction Eq. (5). Lines 3 and 4 correspond to Eq. (3) with a temperature-dependent parameter ζ ; in this case, $a(T)$ is not consistent with the extrapolated behavior near T_c (see Fig. 2)

The scaling behavior (6) is very well confirmed by Monte Carlo data over a wide range of temperatures, giving $y = 0.45 \pm 0.02$ [8,14] instead of the classical droplet model value $y = 1$. Setting $\beta = 5/16$ and $\bar{\delta} = 5$ we then have $\zeta = 2.09$ (in contrast to the classical value $\zeta = 2.2$) and $t = 2.31$ (instead of $t = 1.04$ when $\bar{\nu} = 2/3$ or $t = 1$ when $\bar{\nu} = 0.64$).

Fig. 1 compares the computer simulation data along the coexistence line with the prediction by Eq. (5) when $\zeta = 2.09$, $\alpha = 0.88$ and $a(0.6 T_c) = 1.40$, $a(0.8 T_c) = 0.38$, $a(0.9 T_c) = 0.10$. These values for $a(T)$ are compared with the expectation $a \sim \epsilon^{2.31}$ in Fig. 2. Fig. 2 also includes the values for $a(T)$ obtained by fitting Eq. (3) to the data; these values are seen to be far away from the expectation $a \sim \epsilon^{1.04}$. We thus find that the evidence here, together with the one in Ref. [8], definitely favors the assumptions contained in Eqs. (5) and (6).

ONE-PHASE REGION

The classical droplet model [4,5] predicts that $p_1(h) \sim p_1^S \exp(-h l)$ in the one-phase region; h represents here (in the language appropriate for

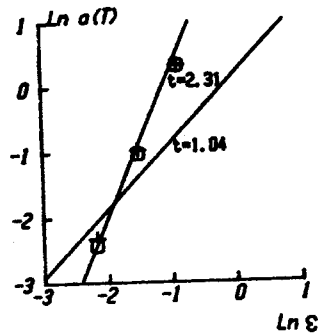


FIG. 2. We compare here the expectations $a \sim \epsilon^t$, $t=1.04$ or $t=2.31$ respectively with the values of $a(T)$ obtained by fitting the computer simulation data with Eq.(3), where τ is allowed a temperature dependence (circles), and with Eq.(5), where $\tau = 2.09$ (crosses). Note that only the consequences from Eq.(5) seem again to be supported by the data.

the spin system) the external magnetic field defining the phase point considered at each T , and $p_1^S = p_1(h=0)$. On the other hand, extending the validity of scaling behavior [6] it follows that $p_1(h) = p_1^S f'(h^{1/y})$ at small h . This scaling property with $y \approx 0.45$ is again confirmed very well by the data corresponding to small fields [8]. More precisely we find (see Fig.3) that

$$p_1(h) / p_1^S \sim \exp(-\eta l) \quad (7)$$

where $\eta \propto h^{1/y}$ for $h < 0.1$ ($h \equiv \mu H / kT$ with the usual notation [8]) while it seems that one rather has the classical prediction $\eta \propto h$ for $h > 0.2$ [7].

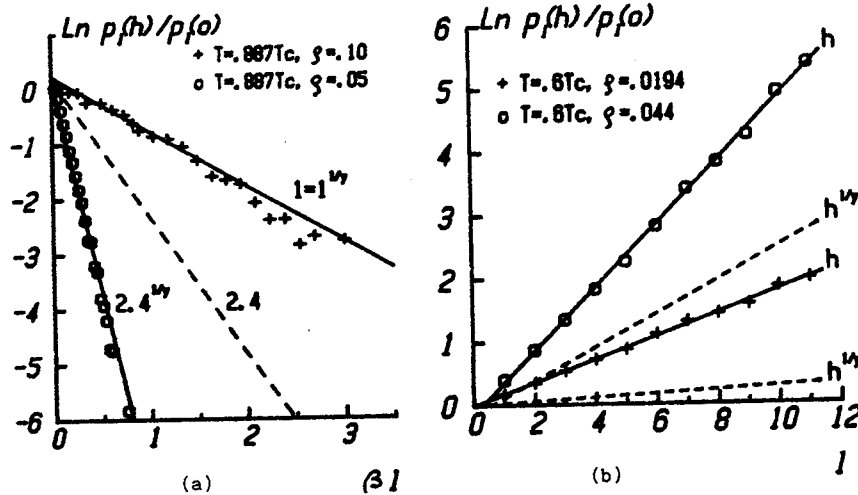


FIG. 3. (a) A test of Eq.(7) to show that $\eta \propto h^{1/y}$ when $h < 0.1$. The graph deals with h_r , the relative field assuming that $h=1$ at $T=0.89T_c$, $\beta = 0.1$. The numbers shown are the slopes of the corresponding lines. Here $\beta = 0.03$. The same situation occurs at other temperatures and small fields. (b) Similar graph when $|h| > 0.2$; data from Ref. [7]. Here $h = -0.2$ ($\beta = 0.019$) and $h = -0.55$ ($\beta = 0.044$); the data rather suggest that $\eta \propto h$.

In order to describe any value of the field in a compact formula, one may assume [9] that $p_1 \approx Q_1 w^1 (1-\phi)^{k_1}$ where $w = w(T, \phi)$ is a renormalized "fugacity" and Q_1 is a "cluster partition function" [8]. Using the exact values computed by M. Sykes for Q_1 up to $l=10$ one may find the adjustable parameters w and k_1 ; we found [8] that $k_1 = 3.25$, $k_2 = 4.5$, $k_3 = 5$, $3 \leq l \leq 10$, independent of T and ϕ , and will assume that $k_1 = 5$ for $l > 10$. The partition functions Q_1 for $l > 10$ can be estimated from Eq.(5),

$$w_1 \equiv Q_1 / Q_{l+1} \approx w \exp \left[-(\phi \ln p_1 / \phi^1)_{l+1/2} \right], \quad (8)$$

so that one may compute $p_1(h)$ in general as

$$p_1 = p_{10} w^{1-l_0} \prod_{l=10}^{l-1} (w_1)^{-1}, \quad l_0 \geq 3. \quad (9)$$

Fig. 1 compares this formula with the computer simulation data. One also has from above:

$$p_1 / p_1^s = (w / w_s)^1 \left[(1-\phi) / (1-\phi_s) \right]^{k_1} \quad (10)$$

where w_s and ϕ_s are respectively the values of w and ϕ at $h=0$.

We finally mention that assuming the factorization of the scaling function $p_1(h)$ it readily follows [8] that $s_1 \sim l^x$ with $x \approx 0.84$. This is also reasonably confirmed by the computer simulation data with $0.81 \leq x \leq 0.90$, slightly changing with temperature. It seems difficult, however, to discard a behavior $s_1 \sim 1 + b l^{2/3}$ with the finite amount of data which is available to us. The latter would imply that the scaling function does not factorize and that $s_1 = l^x f^*(l^z)$, $x \approx 0.84$, $z \approx 0.29$ and that one has $f^* \sim l^{y-z} (1 + b l^{-1/3})$.

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