

Geometrical description of phase transitions in terms of diagrams and their growth function

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Many statistical mechanical models lend themselves to a geometrical description in terms of diagrams built out of elemental units such as bonds, plaquettes, etc. In some cases, these diagrams represent physical systems such as polymers, surfaces, etc., and can be identified occasionally with certain unphysical limits of some spin models. These diagrams exhibit additional transitions, such as percolation, which may not be easily detectable in the original spin model they correspond to. Thus a system of diagrams forms an important statistical mechanical model in its own right, requiring a direct study. We introduce an entropy function S for such a system, which possesses all the thermodynamic properties of an entropy. This entropy function is not the same as the usual entropy of the original statistical model to which the diagram system is related. In particular, the equation of state can be recast in a form so that it can be easily integrated to yield the entropy function, something that may not be easily done for the original model. A knowledge of S allows us to obtain the free energy ω by a Legendre transform. Using this approach, we calculate S and ω for various geometrical objects on a Bethe or a Bethe-like lattice. This then yields a "mean-field" approximation for S and ω for realistic lattices. These include branched polymers and random surfaces among others. The entropy function σ per elemental unit from which diagrams are built gives rise to the growth function $\mu = \exp(\sigma)$, which plays an important role in locating the singularities in the force energy and, hence, the phase transition. We also discuss the relevance of μ for the dilute limit. We illustrate our results by various examples.

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I. INTRODUCTION

The diagrammatic expansion for a variety of physical models which, in general, include high- or low-temperature expansion, strong coupling expansion, or Feynman diagram expansion in continuous field theory, is widely recognized as a powerful tool within the context of statistical mechanics and quantum field theory [1,2]. The cluster theory of Ursell as developed by Mayer to investigate the problem of condensation of a classical gas [3] provides an elegant and compact description of the problem. The high-temperature diagrammatic expansion [1,2] of the Ising model in a field and its careful investigation [4] has recently proved to be quite useful, especially in uncovering percolation transitions which determine the radius of convergence of the diagrammatic expansion. These diagrams are linear in nature as they are made up of edges of the lattice. In general, these diagrams can be identified as representing branched polymers [5,6]. Such identification is, indeed, quite useful, as shown recently [4].

The Feynman diagrammatic expansion [2] in quantum field theory is another elegant example of the power of a geometric description of a physical model. Again, these diagrams are linear, random paths as they are made up of linear segments described by the propagator. The linear nature of the diagrams is a feature of a theory with point-like interactions.

The situation changes when we wish to describe a theory of strings [7]. Because the interaction between strings is no longer localized, one needs to use random

surfaces to represent the theory of strings in terms of diagrams. The diagrams now are random surfaces and not random paths. Random surface representation of lattice gauge theories [2,8] has been very useful. In particular, the representation enables us to draw a subtle but important distinction between the confined and the Higgs phase in a Z_2 lattice gauge theory coupled to matter [9].

The diagrammatic expansion for a physical system involves diagrams which may be "one dimensional," i.e., linear, or "two dimensional," i.e., areal. Linear diagrams are made up of basic units that are one dimensional ($D=1$) while areal (or surface) diagrams are made up of units that are two dimensional ($D=2$). On a lattice, a $D=1$ unit is an edge or a bond of the lattice; a $D=2$ unit is a plaquette. For a continuum theory, a $D=1$ unit is an elemental path and a $D=2$ unit is an elemental surface. The diagrams are obtained by "gluing" together these elemental units according to a set of specific rules. For example, a self-avoiding walk (SAW), also called a linear polymer, is obtained by gluing or joining together bonds ($D=1$) of a lattice, such that no more than two bonds share a given site of a lattice, and no loops are formed. If the last constraint is relaxed, we get self-avoiding walks and loops. If we relax the constraint on the valency of a site and allow for more than two bonds to share a given site, we get self-avoiding branched polymers. Similarly, random surfaces are generated by gluing together plaquettes following some rules. If the rule enforces every bond of the lattice to be shared by either two plaquettes or no plaquettes, then we obtain closed planar surfaces. If we allow a bond to have no more than two plaquettes,

we obtain closed and open surfaces. Thus the topology of the geometrical objects is determined by the dimension of the basic unit and by the set of rules used to generate them.

There are cases [7,10] where one must study geometrical objects obtained from gluing basic units of dimension $D > 2$. Therefore it becomes obvious that a study of geometrical objects ($D \geq 1$) is central to our understanding of a variety of physical systems. In particular, since different systems give rise to a different set of rules governing the formation of these geometrical objects, it is important to investigate the effect of changing rules on the behavior of the geometrical objects which, in turn, will provide us with insights into the behavior of corresponding physical systems. This is our central goal here.

One of the important characteristics of the geometrical picture is the growth function, to be defined more precisely in the next section. Roughly speaking, the growth function describes how the number of configurations increases as the size of the configuration increases, and is related to the entropy function. Because of the latter connection, the growth function plays a very useful role in our investigation. One of the important classes of problems is to understand the behavior of a single geometrical object as it grows. An understanding of a single object is quite useful in understanding the behavior of a large number of objects together. The former case is usually treated as a special limit called the dilute limit of the latter case—the limit in which one probes the behavior of a single object since objects are far apart in the limit. The latter case, in which the number of objects is fluctuating with its average controlled by an activity, corresponds to a grand canonical ensemble. In contrast, the former case is called a canonical ensemble, since the number of objects is fixed (and is equal to unity).

In the (single-object) canonical ensemble, the growth function characterizes the growth of a single object and is an important quantity of physical interest as it determines the singularity of the partition function (see Sec. II). However, even the study of a single object is not trivial and various approximate techniques and exact enumerations have been used to understand the nature of the singularity.

Major progress was made when certain “unphysical” spin systems [11–15] were identified as providing a description of a canonical ensemble of the geometrical objects. The “unphysical” nature of the identification is due to an unphysical limit that must be taken in the prescription. However, in some cases, as discussed recently [16–24], such an unphysical limit violates thermodynamic stability in a certain sense and the implication of this is not well understood. Therefore it is necessary to investigate the canonical ensemble directly without any recourse to the so-called unphysical limit. Indeed, it is this desire that has motivated this investigation.

One of the main reasons for considering graphical description is that geometrical objects can exhibit two kinds of phase transitions [25]. A transition due to a singular free energy is usually called a thermal transition. This transition must be distinguished from percolation [5,6,26], known as a geometrical phase transition, which

is not accompanied by any singularity in the free energy. However, it should be stressed at the outset that the absence of any singularity in percolation is due to a limited parameter space for the model. By extending the parameter space properly, one finds that the extended free energy also exhibits singularities at percolation. Therefore the above distinction between the two kinds of phase transitions becomes blurred. The distinction can be made only when considering the limited parameter space. The occurrence of percolation in the model indicates singularities in an enlarged parameter space. The percolation transition has been studied extensively [5,6,25,26] elsewhere. Therefore we focus our attention here on thermal transitions that are associated with singularities in the free energy.

Our approach here is to study a generic model of geometric objects, obtained by gluing together basic units of any D . However, for the sake of clarity, we will mostly cite, as examples, branched polymers. But the results obtained are true for any D . We do not explicitly specify whether we deal with a canonical or a grand canonical ensemble. Our results are, therefore, valid for both cases. In particular, they are valid for a single-object canonical ensemble.

A configuration Γ of the geometrical objects is characterized by a set $X(\Gamma) = \{x_1, x_2, \dots\}$ of fixed number p of topological quantities. Associated with each topological quantity x_i is an activity K_i . The statistical weight of Γ is $W_N(\Gamma) \geq 0$ on a lattice of size N . The partition function Z_N is obtained by summing $W_N(\Gamma)$ over all distinct configurations and the free energy $\omega_N = \ln Z_N / N$ converges to ω as $N \rightarrow \infty$. In the thermodynamic limit, configurations are characterized by the set of p densities $\phi = (\phi_1, \phi_2, \dots)$, where ϕ_i represents the density corresponding to x_i , and we associate a free energy function $\omega(\phi)$ with such configurations. We show that the maximum of $\omega(\phi)$ gives the free energy ω in the thermodynamic limit. This is our central and most important result, showing that there is a maximization principle for the free energy of a system of geometrical objects, whether we have a canonical ensemble or a grand canonical ensemble. The entropy function $S(\phi)$ is obtained from ω by the usual Legendre transform: $\omega = S(\phi) + \zeta \cdot \phi$ where ζ is the set of chemical potentials $\{\ln K_1, \ln K_2, \dots\}$ and $\zeta \cdot \phi = \phi_1 \ln K_1 + \phi_2 \ln K_2 + \dots$. This is a customary relation between the free energy ω and the entropy S . Hence principles of traditional thermodynamics are observed in their entirety. In particular, the entropy function satisfies all the thermodynamic requirements including the convexity conditions [27]. The maximum of the entropy function occurs when every chemical potential vanishes: $\zeta_i = 0$ or $K_i = 1$. This result is universal and should not be surprising. The entropy \tilde{S} of any system in traditional thermodynamics is a function $\tilde{S}(\tilde{E})$ of the internal energy \tilde{E} and the entropy achieves its maximum value at infinite temperatures, which corresponds to $\beta = 1/T = 0$. Remember that $(-\beta)$ is the chemical potential controlling \tilde{E} .

Since the entropy function obeys the usual thermodynamic conditions, it is sufficient to yield the entire ther-

modynamics of the system. In particular, a knowledge of $S(\phi)$ gives the equilibrium values of ϕ for a given set $\kappa = \{K_i\}$ according to $\xi_i = -\partial S / \partial \phi_i$. Thus singularities in $S(\phi)$ give rise to phase transitions, and the slope at the point of singularity determines the location of the transition. One of our aims here is to look for such singularities in $S(\phi)$ when they occur at $\phi=0$. Consider, for example, the case of a single density ϕ . A transition at $\phi=0$ may occur in a grand canonical ensemble. However, it surely must occur in a canonical ensemble containing a single object as we will demonstrate. Hence the study near $\phi=0$ is pertinent for a single-object system that is of vital interest to us. The slope of $S(\phi)$ at the origin $\phi=0$ is given by the growth function μ at the origin. Hence the value of the activity K at the transition which occurs at $\phi=0$ is determined by the growth function $\mu(0)$. This is an important result and generalizes the result, which is known to hold for a single object, to a grand canonical ensemble in which the transition occurs at $\phi=0$.

If the entropy function has a linear behavior in a region between ϕ_0 and ϕ_1 , then this corresponds to a first-order transition with a jump discontinuity in ϕ from ϕ_0 to ϕ_1 . If $\phi_0=0$, then the growth function must be a constant over the range $(0, \phi_1)$.

We discuss various examples. In some examples, a spin model is reformulated in terms of diagrams. The model can be solved either exactly or using some approximation. We first discuss the model using the spin language and determine its phase diagram. Then we show that the same phase diagram is obtained by considering the diagram picture. From these examples, we begin to get an understanding of the behavior of the growth function $\mu(\phi)$. This is useful information as μ can be easily computed on a finite lattice by exact enumeration [28]. From such enumerations, one can deduce the behavior of μ in the thermodynamic limit, from which one can deduce the nature and the location of the transition.

We also consider some diagram models directly. They include linear and branched polymers and random surfaces. From their solutions on Bethe and Bethe-like lattices, we calculate the entropy function $S(\phi)$ and the free energy ω . These quantities, then, yield the "mean-field" approximation for S and ω for regular lattices and are very useful.

The layout of the paper is as follows. We introduce the generic model in the next section. The thermodynamic considerations are contained in Sec. III. Here, we derive the following four theorems and a corollary.

Theorem 1. The equilibrium state ϕ_M of the system corresponds to the maximization of the free energy function $\omega(\phi)$; $\phi = \phi_M$ gives the location of the global maximum.

Theorem 2. The free energy is a non-negative function such that it vanishes in the vacuum state ($\phi=0$): $\omega(\phi=0)=0$. Furthermore, ω is a nondecreasing function of each of the activities in the model.

Theorem 3. The entropy is continuous and vanishes in the vacuum state $\phi=0$.

Corollary. The maximum of the entropy function

occurs at $\kappa = 1$.

Theorem 4. The growth function is a monotone nondecreasing function of ϕ .

Section III is the central part of the paper and contains proofs for all the results derived in the paper. We discuss various possible forms of $S(\phi)$ and show how to derive the phase diagram from it. We also introduce and discuss the growth function μ .

After a thermodynamic discussion of the generic model, we restrict ourselves to considering the simplest possible case—the case of a single density ϕ controlled by an activity K . This is also the case for all applications that are contained in Secs. IV–IX. The last section contains a short discussion of the results derived here.

II. GENERIC MODEL AND EXAMPLES

Consider a finite lattice of size N . The size is determined by the number of elemental units from which geometrical objects of interest are constructed according to a certain set \mathcal{R} of rules. Let Γ denote a configuration of geometrical objects. Each configuration is characterized by a set $X(\Gamma)$ of topological quantities, the number $P(\Gamma)$ of objects being one of them. Other quantities may be the number $B(\Gamma)$ of elemental units, the number $V_k^{(1)}(\Gamma)$ of k -functional branches of type 1, where k D -dimensional elemental units meet at a $(D-1)$ -dimensional elemental unit, the number $V_k^{(2)}(\Gamma)$ of k -functional branches of type 2, where k D -dimensional elemental units meet at a $(D-2)$ -dimensional elemental unit, . . . the number $L(\Gamma)$ of loops, the number $h(\Gamma)$ of holes, etc. Thus $X(\Gamma)$ is a set with elements $P, B, V_k^{(1)}, V_k^{(2)}, \dots, L, h, \dots$. We require that these elements be topologically independent.

There exists a statistical weight $W_N(\Gamma|\mathcal{R})$ for each configuration Γ . The partition function for the problem is given by

$$Z_{N,\mathcal{R}} = \sum_{(\Gamma|\mathcal{R})} W_N(\Gamma|\mathcal{R}), \quad (2.1)$$

where the sum is over all distinct configurations generated according to \mathcal{R} . In most cases of interest, the statistical weight is determined only by $X(\Gamma)$. In that case, let $\Omega_N(X)$ denote the number of distinct configurations, all of which being characterized by the same set X . Then the partition function can be rewritten as

$$Z_{N,\mathcal{R}} = \sum_{(X|\mathcal{R})} \Omega_N(X|\mathcal{R}) W_N(X|\mathcal{R}). \quad (2.2)$$

Let us illustrate by a few examples.

Example 1. Consider branched polymers with \mathcal{R} indicating that no more than trifunctional branches are allowed. Thus linear chains are allowed in any configuration. Let $X = (P, B, V_1, V_3)$ where V_1 are end points and V_3 are trifunctional branches. Let the statistical weight be given by $\pi^P K^B H^{V_1} w^{V_3}$. Note that P, B, V_1, V_2, V_3, L are not all topologically independent: only four out of six are independent because of the following two topological identities:

$$\sum_{k \geq 1} (2-k)V_k = 2(P-L), \quad (2.3)$$

$$\sum_{k \geq 1} k V_k = 2B . \quad (2.4)$$

The partition function is given by

$$Z_{N, \mathcal{R}} = \sum \Omega_N(P, B, V_1, V_3 | \mathcal{R}) \pi^P K^B H^{V_1} w^{V_3} . \quad (2.5)$$

Example 2. Consider the previous example but impose the additional requirement in \mathcal{R} that only one polymer is allowed, i.e., $P=1$. The choice of π is now superfluous and can be deleted:

$$Z_{N, \mathcal{R}} = \sum \Omega_N(1, B, V_1, V_3 | \mathcal{R}) K^B H^{V_1} w^{V_3} . \quad (2.6)$$

Note that (2.5) does not reduce to (2.6) for $\pi=1$ since \mathcal{R} is different in the two examples. Indeed, for $\pi=1$, we do not care about the number of polymers. Hence we can introduce

$$\Omega_N(B, V_1, V_3 | \mathcal{R}) = \sum \Omega_N(P, B, V_1, V_3 | \mathcal{R}) , \quad (2.7)$$

where the sum is over all possible P consistent with given B, V_1, V_3 , and \mathcal{R} . The partition function for $\pi=1$ can be rewritten now as

$$Z_{N, \mathcal{R}} = \sum \Omega_N(B, V_1, V_3 | \mathcal{R}) K^B H^{V_1} w^{V_3} , \quad (2.8)$$

which differs from (2.6) in that the two Ω_N 's are different.

Example 3. Consider a model of linear polymers with or without wings. Then \mathcal{R} includes the additional requirement that $V_3=0$. Thus w becomes superfluous and can be discarded. The set $X=(P, B, V_1)$ and the partition function becomes

$$Z_{N, \mathcal{R}} = \sum \Omega_N(P, B, V_1 | \mathcal{R}) \pi^P K^B H^{V_1} . \quad (2.9)$$

It should be noted that, instead of enlarging \mathcal{R} to disallow trifunctional branches in example 1, we may leave \mathcal{R} unchanged, but take the limit $w \rightarrow 0+$ in (2.5). For any finite N , there is obviously no difference. But this may not remain true in the thermodynamic limit $N \rightarrow \infty$. Since $V_3=0$ identically in the example here, its average $\langle V_3 \rangle$ also remains zero. On the other hand, $\langle V_3 \rangle$ in the limit $w \rightarrow 0+$ need not be zero in example 1; one may only say that the density ϕ_3 of trifunctional branches must be zero. Therefore, thermodynamically, the two models are equivalent.

Example 4. One may enlarge \mathcal{R} further by not allowing any rings. Now P and V_1 are related: $V_1=2P$; see (2.3). Hence $X=(P, B)$ and the partition function becomes

$$Z_{N, \mathcal{R}} = \sum \Omega_N(P, B | \mathcal{R}) \pi^P K^B . \quad (2.10)$$

Again, one can obtain this example by rewriting (2.9) as follows:

$$Z_{N, \mathcal{R}} = \sum \Omega_N(P, B, L | \mathcal{R}) (\pi H^2) K^B (1/H^2)^L , \quad (2.11)$$

and taking the limit $H \rightarrow \infty$, keeping $\pi H^2 = \pi' = \text{fixed}$. This limit ensures that the loop-forming activity vanishes and that the density of loops, i.e., rings must be zero. This does not ensure that there are no rings present. On the other hand, the form (2.10) ensures that no rings are ever allowed.

If we ignore such a subtle, but thermodynamically irrelevant, difference between the two approaches, then the two descriptions are thermodynamically equivalent.

A word of caution should be given. The limit considered above should not be such that no polymers are allowed. For example, if $\pi=0$, no polymers are allowed and the partition function reduces to unity corresponding to the vacuum state (where no polymers are present). On the other hand, $\pi \rightarrow 0+$ may still allow some polymers, even though their number density will be identically zero. However, such a state can be, indeed, very different from the vacuum state in many respects. In particular, the latter limit can give rise to a nonzero bond density. This density must be identically zero in the case $\pi=0$.

Example 5. Consider a model of self-avoiding closed surfaces. The set \mathcal{R} ensures that two and only two occupied plaquettes touch each other. The set X includes B , the total number of plaquettes, and h , the total number of handles. There is no restriction on the allowed number of surfaces. The statistical weight is given by $K^B \eta^h$ and the partition function is given by

$$Z_{N, \mathcal{R}} = \sum \Omega(B, h | \mathcal{R}) K^B \eta^h . \quad (2.12)$$

Since \mathcal{R} imposes no restriction on the number of surfaces, this is equivalent to $\pi=1$. This does not mean that only a single surface is allowed [see discussion following (2.6)]. To obtain that one must enlarge \mathcal{R} to disallow more than one surface.

Example 6. We can allow open surfaces in example 5 by introducing an additional activity H for a perimeter bond (at which only a single occupied plaquette appears). Let γ denote the total perimeter of all surfaces. The partition function is now given by

$$Z_{N, \mathcal{R}} = \sum \Omega(B, h, \gamma | \mathcal{R}) K^B \eta^h H^\gamma ; \quad (2.13)$$

if we do not care about the number of handles, we can set $\eta=1$ and introduce

$$\Omega(B, \gamma | \mathcal{R}) = \sum_{(h)} \Omega(B, h, \gamma | \mathcal{R}) , \quad (2.14)$$

where the sum is over all possible h consistent with B and γ and with the set \mathcal{R} of rules [see discussion following (2.6)]. Then the partition function becomes

$$Z_{N, \mathcal{R}} = \sum \Omega(B, \gamma | \mathcal{R}) K^B H^\gamma . \quad (2.15)$$

III. THERMODYNAMICS

Let us turn back to (2.2) and let X_M denote the set X at which the summand $\Omega_N(X | \mathcal{R}) W_N(X | \mathcal{R})$ attains its maximum value. The set X_M obviously depends explicitly on κ . However, we do not exhibit this dependence explicitly in the following. For the sake of brevity, we will also suppress \mathcal{R} in the following. It is clear that

$$\alpha_N(X) = \Omega_N(X) W_N(X) / \Omega_N(X_M) W_N(X_M) \leq 1 . \quad (3.1)$$

Let p denote the fixed number of elements x_1, x_2, x_3, \dots of X . (The number p must not change as N changes.) Since each x_k takes integer values which are bounded

above by $C_k N$, where C_k is a constant independent of N , the possible number of terms in the sum (2.2) is bounded above by $C N^p$, where $C = C_1 C_2 C_3 \cdots C_p$. Thus

$$\sum_{(X)} \alpha_N(X) \leq C N^p. \quad (3.2)$$

Let us rewrite (2.2) as follows:

$$Z_N = \Omega_N(X_M) W_N(X_M) \sum_{(X)} \alpha_N(X).$$

The “free energy per elemental unit” is given by

$$\begin{aligned} \omega_N &= \ln Z_N / N \\ &= \frac{1}{N} \left[\ln \Omega_N(X_M) W_N(X_M) + \ln \left[\sum_{(X)} \alpha_N(X) \right] \right]. \end{aligned} \quad (3.3)$$

The last term is evidently bounded above; see (3.2). Hence, as $N \rightarrow \infty$, this term converges to zero. Therefore the thermodynamic limit $N \rightarrow \infty$ of ω_N is determined only by the first term, i.e., by the set X_M . In order to facilitate taking the thermodynamic limit, we introduce the set of thermodynamic densities

$$\begin{aligned} \phi &= \lim_{N \rightarrow \infty} (X/N) = \lim_{N \rightarrow \infty} [x_1/N, x_2/N, x_3/N, \dots] \\ &= (\phi_1, \phi_2, \phi_3, \dots), \end{aligned} \quad (3.4)$$

where

$$\phi_k = \lim_{N \rightarrow \infty} (x_k/N). \quad (3.5)$$

The density set corresponding to X_M is denoted by ϕ_M :

$$\phi_M = (\phi_{1M}, \phi_{2M}, \phi_{3M}, \dots). \quad (3.6)$$

Let

$$\omega(\phi_M) = \lim_{N \rightarrow \infty} \frac{1}{N} \ln [\Omega_N(X_M) W_N(X_M)]. \quad (3.7)$$

Since ϕ_M is an explicit function of parameters determining W_N , $\omega(\phi_M)$ is an implicit function of these parameters. If these parameters are the activities K_1, K_2, \dots , etc. [see (3.10) below], then $\omega(\phi_M)$ is an implicit function of these activities. Now, as $N \rightarrow \infty$, we have

$$\omega_{N \rightarrow \infty} = \omega(\phi_M), \quad (3.8)$$

which is our central result. In order to fully appreciate this result, let us introduce the free energy function

$$\omega(\phi) = \lim_{N \rightarrow \infty} \frac{1}{N} \ln [\Omega_N(X) W_N(X)], \quad (3.9)$$

where the limit is taken at a fixed ϕ . Then the content of (3.7) can be stated as the following.

Theorem 1. The equilibrium state ϕ_M of the system corresponds to the maximization of the free energy function $\omega(\phi)$; $\phi = \phi_M$ gives the location of the global maximum.

This is our fundamental result. The triviality of the proof should not lessen the importance and significance of the result. Note that ϕ corresponds to densities per-

taining to the geometrical objects and not to the original (spin) degrees of freedom of the model this geometrical description applies to. What we have demonstrated here is the following: there is an equivalent maximization principle of the “free energy function” $\omega(\phi)$ in terms of diagrams. Note that our free energy definition (3.3) lacks the conventional minus sign; hence our free energy is maximized rather than minimized.

The actual free energy ω for a given κ is given by the maximum of the function $\omega(\phi)$. In the following, we will use the term free energy function for $\omega(\phi)$ and reserve the term free energy for ω , which is the equilibrium value of the free energy for a given κ .

It is worth noting that Z_N is a sum of non-negative terms. Therefore it is an increasing function of its activities K_i . Furthermore, since the statistical weight W_N for the “vacuum” state ($x_i = 0$ for all i) is identically equal to unit, $Z_N \geq 1$. Hence the free energy is always non-negative. Furthermore, $\phi_i = 0$ when $\kappa_i = 0$. Hence the free energy vanishes at $\kappa = 0$: $\omega(\kappa = 0) = 0$. Thus we have the following theorem.

Theorem 2. The free energy is a non-negative function such that it vanishes in the vacuum state ($\phi = 0$), i.e., when $\kappa = 0$. Furthermore, ω is a nondecreasing function of each of its activities.

Since the free energy must be maximized, all required thermodynamic stability requirements must be met by the free energy ω . In particular, since we did not specify \mathcal{R} , the thermodynamic stability must be enjoyed by ω even when we consider a single object. As we will see later, this has not always been appreciated.

So far, no special forms of $\Omega_N(X)$ and $W_N(X)$ have been taken. Therefore the above theorem is a general thermodynamic principle. Let us now specialize to a simple form of W_N such as has been used in various examples in Sec. II. Let κ denote the set of activities corresponding to the set X and let

$$W_N(X) = \kappa^X \equiv \prod_i K_i^{x_i}, \quad (3.10)$$

where K_i are various elements of κ . For example, $\kappa = (\pi, K, H, W)$ and $X = (P, B, V_1, V_3)$ in (2.5). From (3.9), we have

$$\omega(\phi) = S(\phi) + \xi \cdot \phi, \quad (3.11)$$

where ξ denotes the set of “chemical potentials”

$$\xi = (\xi_1, \xi_2, \dots), \quad \xi = \ln K_i. \quad (3.12)$$

and $\xi \cdot \phi$ stands for $\xi_1 \phi_1 + \xi_2 \phi_2 + \xi_3 \phi_3 + \dots$. The new function $S(\phi)$ is the “entropy function” defined by

$$S(\phi) = \lim_{N \rightarrow \infty} \frac{1}{N} \ln \Omega_N(X), \quad (3.13)$$

where the limit is taken at a fixed ϕ . The entropy function $S(\phi)$ denotes the entropy per elementary unit in the lattice in our geometrical description and should not be confused with the entropy of the original (spin) model this geometrical description pertains to.

From (3.13), we observe that the entropy is an explicit function only of ϕ but not of κ . On the other hand, the

free energy must be an explicit function only of κ as is evident from (3.3) since the partition function is a function only of κ . Therefore, in equilibrium, (3.11) becomes a Legendre transform

$$\omega(\kappa) = S(\phi) + \zeta \cdot \phi . \tag{3.14}$$

In other words, one can use ϕ in our thermodynamic description by considering the entropy or use κ in our thermodynamic description by considering the free energy; the relation between the two is given by the Legendre transform.

For every finite N , the free energy ω_N is a continuous and a convex [27] function of ζ . Thus its limit $\omega(\kappa)$ also retains these properties. From (3.14), this implies that $S(\phi)$ is a continuous function.

From (3.14), we note that

$$\frac{\partial \omega}{\partial \zeta_i} = \phi_i , \tag{3.15}$$

as it should be. On the other hand, $\partial \omega / \partial \phi_i = 0$ in equilibrium and gives

$$\zeta_i = - \frac{\partial S}{\partial \phi_i} . \tag{3.16}$$

Whether we are considering the equilibrium state or not will be evident from the discussion. Therefore, from now on, we will not explicitly use the subscript M to denote equilibrium states unless it is needed for clarity.

From the vanishing of ω in the vacuum state, we find that $S(\phi) = 0$ at $\phi = 0$. Thus we obtain the following theorem.

Theorem 3. The entropy is continuous over the allowed range of ϕ and vanishes in the vacuum state $\phi = 0$.

From (3.16), we note that the maximum of the entropy corresponds to $K_i = 1$ for all i , thus giving us the following corollary.

Corollary. The maximum of the entropy function occurs at $\kappa = 1$.

Let us now introduce the concept of the growth function. Consider a single object and imagine characterizing it by only one topological quantity which is its size B , the number of elemental units which make up the object. Let $\Omega_N(B)$ denote the number of distinct configurations the object possesses on the lattice. It is usually the case that in the thermodynamic limit $N \rightarrow \infty$, such that $\phi = B/N$ is kept fixed, the ratio

$$\frac{\Omega_N(B+1)}{\Omega_N(B)}$$

approaches a limit $\mu(\phi)$ which depends on ϕ . Therefore one can introduce the quantity

$$\mu_N(B) = [\Omega_N(B)]^{1/B} , \tag{3.17}$$

such that it approaches the same limit $\mu(\phi)$ as $N \rightarrow \infty$, keeping $B/N = \phi$ fixed. It is evident that $\mu(\phi)$ is related to the entropy according to

$$S(\phi) = \phi \ln \mu(\phi) . \tag{3.18}$$

The quantity $\mu(0)$ at $\phi = 0$ corresponds to the ‘‘growth

rate’’ for the geometrical object as it becomes infinitely large, while covering a zero fraction of the lattice. In this regard, it also represents the ‘‘growth rate’’ for the object as it grows on an infinite lattice. There is one complication. On an infinite lattice, the number of distinct configurations is always infinitely large as the object can be placed anywhere on the lattice by simple translation. To avoid this problem, we must ‘‘root’’ the object.

The growth function $\mu(\phi)$ can be introduced in the same fashion as above even when there is more than one object.

We also know from (3.14) that

$$\ln K \mu(\phi) = \omega / \phi \geq 0 , \tag{3.19}$$

where ω is the (equilibrium) free energy per elementary unit and where K is the activity controlling the elementary unit. The use of (3.16) shows that

$$S' = \ln \mu(\phi) + \phi \mu'(\phi) / \mu(\phi) = - \ln K .$$

Hence,

$$\ln K \mu = - \frac{\phi \mu'(\phi)}{\mu(\phi)} \geq 0 ,$$

because of (3.19). Therefore we conclude that

$$\mu'(\phi) \leq 0 , \tag{3.20}$$

and that

$$\omega = - \phi^2 \mu'(\phi) / \mu(\phi) \geq 0 . \tag{3.21}$$

This yields the following important theorem.

Theorem 4. The growth function is a monotone nonincreasing function of ϕ .

We can also introduce a set of growth functions $\mu_i(\phi_1, \phi_2, \phi_3, \dots)$ as follows in the case X contains more than one quantity x_1, x_2, \dots . We consider the ratio

$$\frac{\Omega_N(x_1, \dots, x_i + 1, x_{i+1}, \dots)}{\Omega_N(x_1, \dots, x_i, x_{i+1}, \dots)} ,$$

as $N \rightarrow \infty$, such that $x_i/N = \phi_i$ is kept fixed. The ratio is expected to reach a limit $\mu_i(\phi_1, \phi_2, \phi_3, \dots)$ describing the growth of the object with respect to its i th topological quantity x_i . We can construct the quantity

$$\mu_{i,N} = [\Omega_N(x_1, \dots)]^{1/x_i} . \tag{3.22}$$

As $N \rightarrow \infty$, such that $x_i/N = \phi_i$ is kept fixed, the sequence $\mu_{i,N}$ converges to $\mu_i(\phi_1, \phi_2, \phi_3, \dots)$ introduced above. Furthermore,

$$S(\phi) = \phi_i \ln \mu_i(\phi) \text{ (no summation)} , \tag{3.23}$$

which represents a generalization of (3.18).

We can get a better feeling for μ by rewriting (3.18). Let us introduce entropy per basic unit on the diagram

$$\sigma = S(\phi) / \phi . \tag{3.24}$$

In terms of σ ,

$$\mu = \exp(\sigma) . \tag{3.25}$$

Thus μ represents the ratio of the number of new

configurations generated and the number of old configurations when an additional basic unit is added to the diagram. This quantity can be defined for all ϕ , and need not be restricted to $\phi \rightarrow 0$, i.e., the dilute limit.

From the above, it is obvious that μ must vanish as ϕ takes its maximum possible value. Further, it is not hard to understand why μ must be a nonincreasing function of ϕ : Because of excluded-volume effects, it becomes harder and harder to generate new configurations from old ones as ϕ increases.

IV. PHASE TRANSITIONS

The presence of a singularity in the free energy $\omega(\kappa)$ determines the existence and the nature of a phase transition in the model. Since the entropy is related to the free energy through a Legendre transform and since the transform does not alter the singularity, the singularity of ω must also be present in S . However, these are exceptions. In some cases, the singularity in S may be at the boundary of the ϕ space. In that case, the singularity in S may remain hidden and may require careful analysis. With this warning, we may focus our attention on S rather than on ω . This is what we wish to do in the following.

To simplify our discussion further, we restrict ourselves to X containing only one topological characteristic, to be denoted by B , in the following. The corresponding activity is denoted by K . The activity space corresponds to $0 \leq K \leq \infty$. We will assume that the singularity in $\omega(K)$, if there is one, occurs at a nonzero and finite K . We will assume that the density set ϕ also contains only one element, viz., the density corresponding to B , and will be simply denoted by ϕ . The density space corresponds to $0 \leq \phi \leq \phi_{\max}$ where ϕ_{\max} is the maximum allowed value of ϕ , which is usually finite. However, it is easy to extend the entire discussion to more than one element in X and ϕ .

The partition function is given by

$$Z_N = \sum_{B \geq 0} \Omega_N(B) K^B. \quad (4.1)$$

The average $\langle B \rangle_N$ is given by

$$\langle B \rangle_N = \sum B \Omega_N(B) K^B / Z_N = (\partial / \partial \zeta) \ln Z_N \geq 0, \quad (4.2)$$

where $\zeta = \ln K$. In the thermodynamic limit, the density ϕ is given by

$$\phi = \lim_{N \rightarrow \infty} \frac{1}{N} \langle B \rangle_N = \frac{\partial \omega}{\partial \zeta} \geq 0. \quad (4.3)$$

Here, we are assuming that the derivative $\partial / \partial \zeta$ and the thermodynamic limit $N \rightarrow \infty$ can be interchanged.

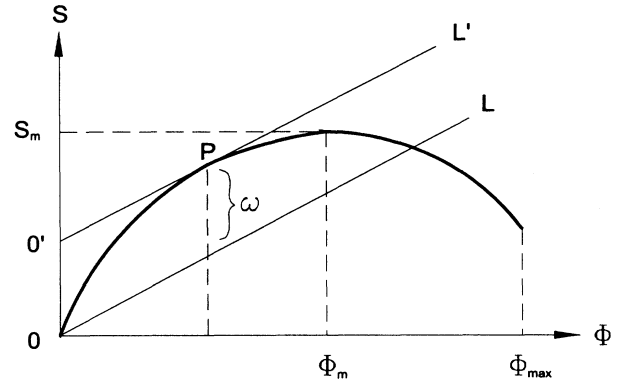
It is easy to see that $\partial^2 \omega_N / \partial \zeta^2$ is related to the average of the square of the fluctuation $B - \langle B \rangle_N$; hence it must be non-negative. Therefore we have

$$\frac{\partial \phi}{\partial \zeta} = \frac{\partial^2 \omega}{\partial \zeta^2} \geq 0, \quad (4.4)$$

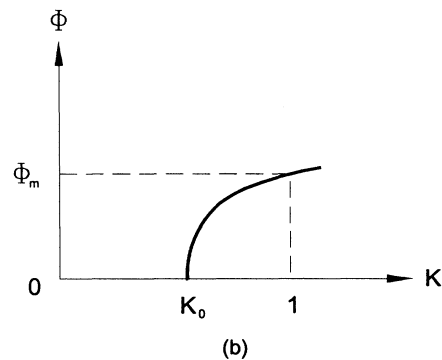
On the other hand, since $\zeta = -\partial S / \partial \phi$, we have

$$\frac{\partial^2 S}{\partial \phi^2} \leq 0. \quad (4.5)$$

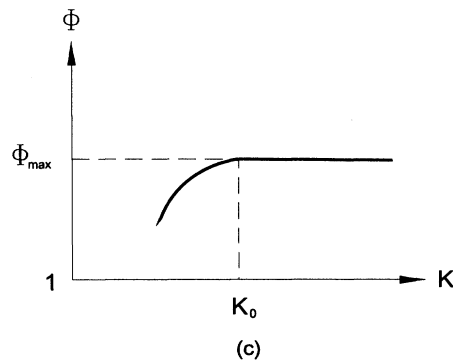
Therefore the equilibrium entropy must have a nonpositive curvature. This is the required stability or convexity criterion for the equilibrium entropy; see Fig. 1(a). However, there are examples, where the convexity rule is violated [see Fig. 2(a)], as we will see later. Therefore the region of ϕ over which the convexity condition is violated is unphysical. To construct a convex hull [27] [Fig. 2(a)] for such an entropy function is a standard technique in thermodynamics and, as we will see below, corresponds



(a)



(b)



(c)

FIG. 1. (a) Analytic and convex entropy function with a possible phase transition near $\phi=0$ and $\phi=\phi_{\max}$; the schematic form of density ϕ near (b) $\phi=0$ and (c) $\phi=\phi_{\max}$.

to a first-order transition. The convex hull is called the entropy in the following and corresponds to the entropy hull in equilibrium. In contrast, the entropy function may give rise to a convexity violation.

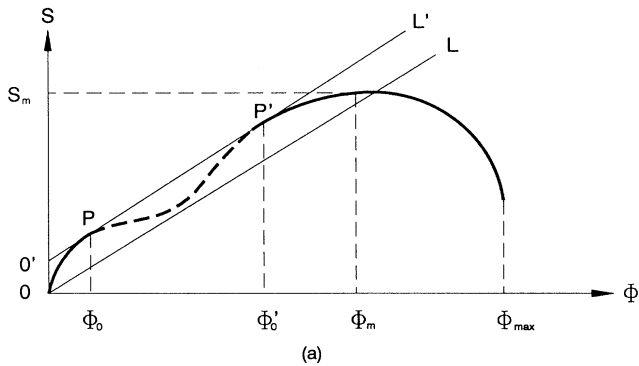
A characteristic property of a convex hull formed out of an entropy function (which violates convexity) is that there is a range of ϕ over which the entropy has the same slope. This is seen easily from Fig. 2(a).

It should be noted that the entropy function may be analytic even when it contains a region over which convexity is violated. However, the convex hull is a singular function, the singularity describing a first-order transition. In the following, we will always mean the convex hull when talking about the entropy. As said above, the hull represents the equilibrium entropy.

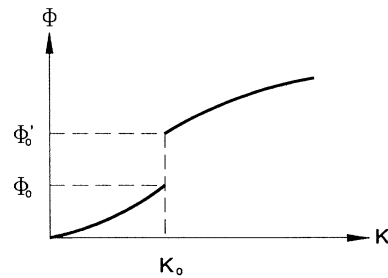
Let us consider the Legendre transform (3.14) from S to ω . The geometrical content of the transform is the following. Draw a straight line OL through the origin [see Figs. 1(a) and 2(a)] of slope $m = -\zeta$. The difference $S - m\phi$ of the entropy and the straight line OL at ϕ gives the free energy ω . Since $\omega \geq 0$ (Theorem 2), the segment of the entropy above OL determines the physical state P . The free energy for this state is the maximum.

To determine P graphically, we move OL parallel to it until it touches the entropy function at P [see $O'L'$ in Figs. 1(a) and 2(a)]. The free energy at P is given by the intercept OO' . This free energy is the maximum possible value of ω at the given K , i.e., ζ .

In Fig. 2(a), $O'L'$ touches S at two points, P and P' ,



(a)



(b)

FIG. 2. (a) Entropy function with a region of nonconvexity shown by broken segment PP' and associated first-order phase transition at which (b) the density is discontinuous at K .

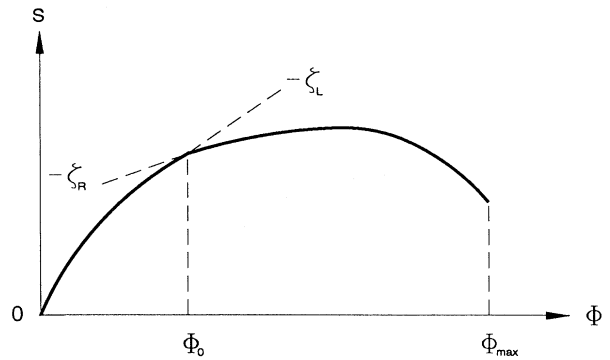
both having the same free energy OO' . Therefore both represent equilibrium states. This situation corresponds to a first-order transition at $K = K_0$, where $\zeta_0 = -\ln K_0 = -m$, m being the slope of $O'L'$. For $K < K_0$, the physical states belong to the segment OP of S . For $K > K_0$, the physical states belong to the segment past P' . Thus we have that there must be a first-order transition if the entropy function gives rise to the violation of convexity over a finite range. The convex hull is given by the segment OP , the straight line PP' , and the segment of S past P' , and represents a singular function.

Let us now consider various possible forms of equilibrium S which, as said earlier, must be convex, and discuss the nature of the transition they represent. Since ϕ is a monotone increasing function of K [see (4.4)], it is obvious that $\phi = \phi_{\max}$ as $K \rightarrow \infty$. Similarly, $\phi \rightarrow 0$ at $K \rightarrow 0$.

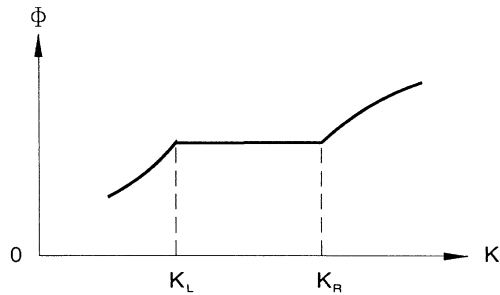
(a) The entropy function is analytic and convex over the entire range $(0, \phi_{\max})$, as shown in Fig. 1(a). This does not mean that there can be no phase transition. The phase transition can still occur but only at the end points $\phi = 0$ or $\phi = \phi_{\max}$. The existence of the phase transition depends upon the slopes at the two end points.

First consider $\phi = 0$ and let $S'(0)$ be finite. Since S achieves its maximum at $K = 1$ (see the corollary), the slope at the origin must be positive. The transition occurs at $K = K_0$ given by

$$S' = -\zeta_0 = -\ln K_0 . \tag{4.6}$$



(a)



(b)

FIG. 3. (a) Entropy function with a discontinuous slope at $\phi = \phi_0$ and (b) schematic density profile with two continuous phase transitions at K_L and K_R .

Since $S'(0) = S/\phi$ as $\phi \rightarrow 0$, we also have

$$(\omega/\phi)_{\phi=0} = S'(0) + \xi_0 = 0,$$

from (3.14). From (3.19), we have

$$\ln K_0 \mu(0) = (\omega/\phi)_{\phi=0} = 0 \quad (4.7)$$

for the transition at $\phi=0$. Hence

$$K_0 = 1/\mu(0). \quad (4.8)$$

The relation clearly shows the importance of the growth function $\mu(\phi)$, and, in particular, of $\mu(0)$.

The transition at $\phi=0$ is always continuous. For $K \leq K_0$, $\phi=0$ is the physical state. For $K > K_0$, $\phi > 0$ with ϕ changing continuously. The behavior of ϕ is shown schematically in Fig. 1(b).

Now consider the possibility of a transition at $\phi = \phi_{\max}$. Let $S'(\phi_{\max})$ be finite. Again, the transition occurs at $K = K_0$ given by (4.6), except that the derivative is evaluated at $\phi = \phi_{\max}$. The behavior of ϕ near K_0 is shown in Fig. 1(c).

We can combine both cases and express K_0 in terms of μ as follows:

$$K_0 = \frac{1}{\mu(\phi_0)} \exp \left[-\phi_0 \frac{\mu'(\phi_0)}{\mu(\phi_0)} \right], \quad (4.9)$$

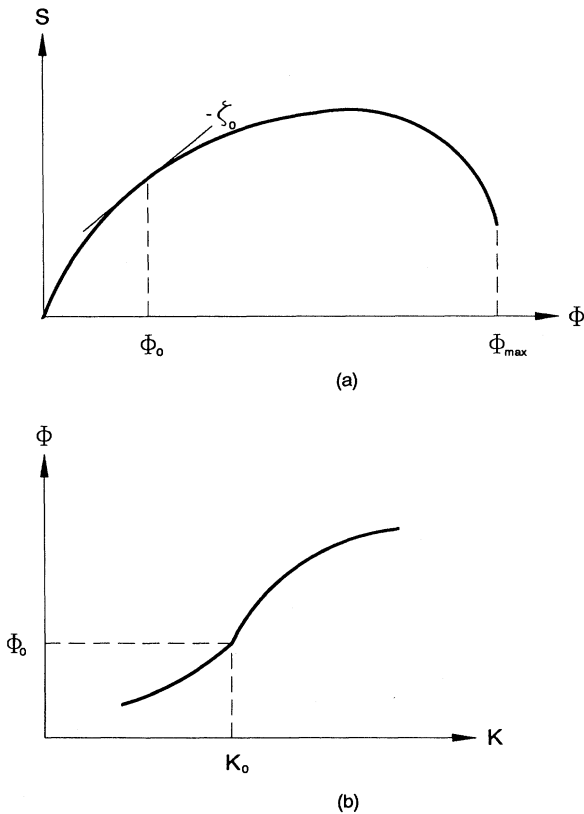


FIG. 4. (a) Entropy function with a singularity at $\phi = \phi_0$ and (b) density singularity at a continuous phase transition at $K = K_0$.

where $\phi = \phi_0$ is the value of ϕ at the transition.

(b) The entropy is nonanalytic in that there is a finite range over which it is linear as shown in Fig. 2(a). In this case, there is a first-order transition from $\phi = \phi_0$ to $\phi = \phi'_0$ at $K = K_0$ given by the slope of $O'L'$ which touches S at P and P' . At the transition, we have

$$\phi_0 \ln K_0 \mu(\phi_0) = \omega_{tr} = \phi'_0 \ln K_0 \mu(\phi'_0) \quad (4.10)$$

according to (3.19). The behavior of ϕ is shown schematically in Fig. 2(b).

(c) There exists a point $\phi = \phi_0$ at which the left and right derivatives of S are different:

$$\Delta S'(\phi_0) = S'(\phi \rightarrow \phi_0^-) - S'(\phi \rightarrow \phi_0^+) > 0,$$

as shown in Fig. 3(a). The two slopes determine K_L and K_R , respectively.

For $K_L < K < K_R$, $\phi = \phi_0$ remains constant. Thus there are two continuous transitions at K_L and at K_R , respectively. The behavior of ϕ near the range (K_L, K_R) is shown schematically in Fig. 3(b).

(d) At $\phi = \phi_0$, S' exists but S is singular. This gives rise to a continuous transition as shown in Fig. 4.

One can construct various combinations out of these cases to construct all possible forms. We will not pause here to do that.

The entropy possesses a singularity inside the domain $(0, \phi_{\max})$ over which it is defined in all cases, except the

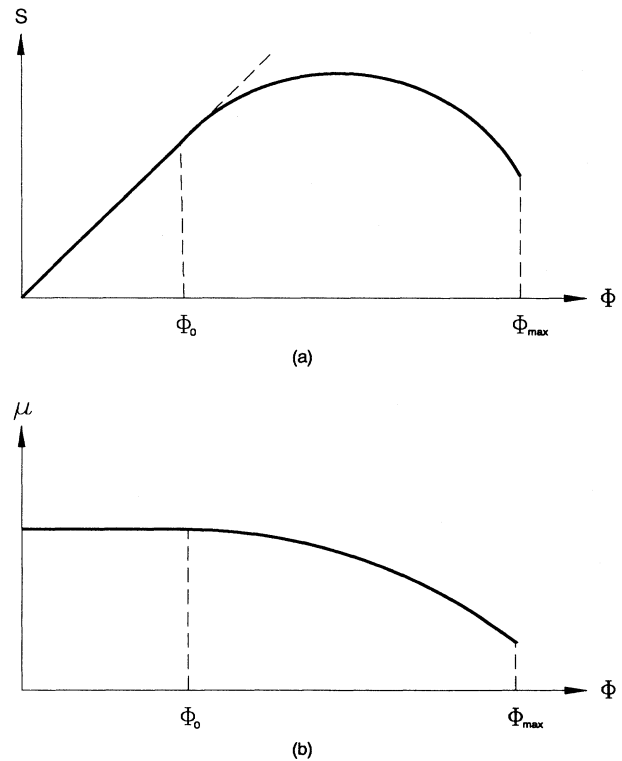


FIG. 5. (a) Entropy function with a linear segment near the origin and (b) associated growth function constant over this range $(0, \phi_0)$.

case (a). In that case, the singularity may occur at the boundary of the domain ($\phi=0$ or $\phi=\phi_{\max}$) and is hidden. The possibility of a phase transition is restricted, therefore, either at $\phi=0$ or at $\phi=\phi_{\max}$. The existence of the transition depends on the slope at the two end points.

In the following, we will consider numerous examples to illustrate various results obtained above. One of the most important results deals with a single-object partition function. If the slope $S'(0)$ is finite at the origin, then the transition occurs at $K=K_0$ given by (4.8). However, whether the transition is first order or second order is determined not by the magnitude of $\mu(0)$, but by whether the entropy has a straight portion over a finite range. If the entropy has a linear portion [see Fig. 5(a)], over a finite range $\Delta\phi=(0, \phi_0)$ then

$$S(\phi) = m\phi = \phi \ln \mu(\phi)$$

ensures that

$$\ln \mu(\phi) = m = -\ln K_0. \tag{4.11}$$

Therefore, whether the transition is first order or second order is determined not by the value $\mu(0)$ but by whether $\mu(\phi)$ is a constant over a finite range $\Delta\phi$. This is shown in Fig. 5(b). The transition point is given by (4.8) for both cases.

V. RANDOM BOND PERCOLATION

Our first example is the simplest possible example where computations can be done exactly in any dimension on any lattice. The problem is that of random bond percolation [5,6,26]. The problem is to study [25] the partition function (4.1) with no restriction on how the bonds are occupied (or unoccupied): One randomly occupies or unoccupies bonds in equilibrium with “*a priori* equal probability.” The computation of $\Omega_N(B)$ is trivial:

$$\Omega_N(B) = \binom{N}{B}, \tag{5.1}$$

where N is the number of bonds on the lattice, out of which B are occupied. Thus, as $N \rightarrow \infty$, such that $B/N = \phi$ is a constant, we have

$$S(\phi) = -[\phi \ln \phi + (1-\phi) \ln(1-\phi)], \tag{5.2}$$

and

$$\mu(\phi) = \frac{(1-\phi)^{1-1/\phi}}{\phi} \geq 0, \tag{5.3}$$

with ϕ lying in the range $(0,1)$.

The entropy is an analytic and convex function, as is evident from the simple form (5.1). Therefore there can be no phase transition except possibly at $\phi=0$ or $\phi=1$, where the entropy vanishes. However, as we will see below, the slopes at the end points are not finite. Hence there is no phase transition in the model (except percolation which is a geometric transition with no singularity in the free energy). The entropy has its maximum at $\phi=\frac{1}{2}$. As we will see below, this will correspond to $K=1$. This is consistent with our corollary.

Let us evaluate $S'(\phi)$ and $\mu'(\phi)$:

$$S'(\phi) = -\ln \left[\frac{\phi}{1-\phi} \right], \tag{5.4}$$

$$\mu'(\phi) = [\mu(\phi)/\phi^2] \ln(1-\phi) \leq 0. \tag{5.5}$$

We observe that $\mu'(\phi) \leq 0$, as it should be (see Theorem 4). From (5.4) and (3.16) we find

$$\phi = K/(1+K). \tag{5.6}$$

Since ϕ denotes the density of occupied bonds, it also represents the probability with which bonds are occupied on the lattice. At $K=1$, $\phi=\frac{1}{2}$, at which the entropy is a maximum, as said above. The bond density is an analytic function of K . The equilibrium free energy

$$\omega = S + \phi \ln K = \ln(1+K), \tag{5.7}$$

and is analytic. Therefore there is no phase transition. This implies that the slope of S at $\phi=0$ and $\phi=1$ must not be finite, as can be easily seen from (5.4).

The behavior of μ near $\phi=0$ and $\phi=1$ is interesting. Near $\phi=0$,

$$\mu(\phi) \sim \frac{e^{1-\phi}}{\phi} \rightarrow \infty \text{ as } \phi \rightarrow 0;$$

the slope also diverges:

$$\mu' \sim \frac{e^{1-\phi}}{\phi^2} \rightarrow -\infty \text{ as } \phi \rightarrow 0.$$

At $\phi=1$, $\mu(\phi)=1$ and $\mu'(\phi) \rightarrow -\infty$.

The following discussion is intended to show how percolation is different from thermal transitions. As is well known, the percolation threshold p_c depends on the geometry of the lattice. On the other hand, there is no such dependence in the entropy $S(\phi)$ in (5.2). Therefore the onset of percolation is not determined by any property of $S(\phi)$ alone, whereas we know that $S(\phi)$ alone is sufficient to determine all thermodynamic properties of the system.

VI. SELF-AVOIDING WALKS

This is somewhat more complicated than the problem of random bond percolation and cannot be solved exactly except in one dimension. We are interested in the partition function (2.10); thus no rings are allowed. We rewrite the partition function in the following form:

$$Z_N = \sum \Omega_N(B,P) K^B (H^2)^P, \tag{6.1}$$

where we have used the fact that $V_1=2P$ denotes the end points of P SAW's which model polymers and K and H represent the activities for a bond formation and an end point respectively. The self-avoiding constraint ensures that no more than two bonds of a walk meet at a given site. Note that the bonds of walks are the occupied bonds on the lattice.

It has been known for quite some time [5,29-31] that one can obtain (6.1) by considering the $n=0$ limit of an n -component spin model: K is related to the nearest-

neighbor coupling βJ and H is related to the external magnetic field βh , where β is the inverse temperature. As usual, the critical behavior in the spin model occurs at a critical point $K=K_c$, $H=0$. As $H \rightarrow 0$, the model (6.1) describes a polymer system with a vanishing number density ϕ_p . This corresponds to the dilute limit. In this limit, there is only one density, the bond density ϕ , characterizing the polymer system. Therefore the study of polymer systems with a given ϕ , with $\phi_p \rightarrow 0$, can be accomplished by studying the spin model as $H \rightarrow 0$. In particular, we wish to determine $S(\phi)$ and $\mu(\phi)$ by considering the spin model first. We will demonstrate, later on, that the same conclusions are obtained by considering the equivalent polymer picture.

To begin with, we first consider a single polymer of size B on a one-dimensional lattice of size N with a periodic boundary. The computation of $\Omega_N(B)$ is trivial:

$$\Omega_N(B) = N. \quad (6.2)$$

Therefore it is evident that

$$S(\phi) = 0, \quad \mu(\phi) = 1, \quad 0 \leq \phi \leq 1. \quad (6.3)$$

Since the entropy is linear, it gives rise to a first-order transition from $\phi=0$ to $\phi=1$ at $K=1$. Since the transition occurs at $\phi=0$, the growth function is a constant, as expected.

We now turn to our model (6.1) in the limit $H \rightarrow 0$. The mean-field calculation of the free energy of the spin model in terms of the magnetization M has been derived elsewhere [30]. The free energy per bond is given by

$$\omega = -KM^2 + (2/q) \ln[1 + K^2 q^2 M^2 / 2], \quad (6.4)$$

where q is the coordination number of the lattice. The equilibrium value of M is obtained by maximizing ω . This yields

$$M = kM / (1 + k^2 M^2), \quad (6.5)$$

where

$$k = Kq. \quad (6.6)$$

The solutions for M are

$$M = \begin{cases} 0, & k < 1, \\ \sqrt{2(k-1)}/k, & k > 1, \end{cases} \quad (6.7)$$

where only non-negative M is chosen since $H \rightarrow 0+$. We see that M is continuous but singular at $k=1$; hence there is a continuous phase transition at $k=1$. Let us consider (6.4) carefully. The free energy ω can be expressed in terms of the usual entropy $\tilde{S}(\tilde{E})$ and the energy \tilde{E} of the spin model. [Note that the free energy ω differs from the usual free energy in that our definition lacks the customary factor of $-T$; see (3.3).] The first term in (6.4) gives $-\beta\tilde{E}$ and the second term gives the entropy \tilde{S} :

$$\beta\tilde{E} = KM^2; \quad (6.8)$$

$$\begin{aligned} \tilde{S} &= (2/q) \ln[1 + K^2 q^2 M^2 / 2] \\ &= (2/q) \ln[1 + \beta K q^2 \tilde{E} / 2], \end{aligned} \quad (6.9)$$

where β is the inverse temperature of the spin system and $\omega = \tilde{S} - \beta\tilde{E}$. Note that the role of the "chemical potential" for the spin system is played by $-\beta$ since

$$\partial\tilde{S} / \partial\tilde{E} = \beta. \quad (6.10)$$

It is easy to see that for (6.10) to be fulfilled, we must have

$$1 + \beta K q^2 \tilde{E} / 2 = 1 + K^2 q^2 M^2 / 2 = Kq \quad \text{for } \tilde{E} \neq 0,$$

which is identical to (6.5). As $\tilde{E} \rightarrow 0$, $\tilde{S} \rightarrow 0$ and we have $\partial\tilde{S} / \partial\tilde{E} = \tilde{S} / \tilde{E} = \beta k$. Comparison with (6.10) shows that $k=1$. For $k < 1$, (6.10) has no meaning and the equilibrium state is given by $\omega=0$, i.e., $\tilde{E} = \tilde{S} = 0$. Thus we reconfirm the phase transition at $k=1$.

We now turn to the polymer picture. We express every quantity in terms of ϕ . From $\phi = k \partial\omega / \partial k$, we find that $\phi = KM^2$. Hence,

$$\phi = \begin{cases} 0, & k < 1, \\ 2(k-1)/kq, & k \geq 1. \end{cases} \quad (6.11)$$

Since ϕ is continuous but singular at $k=1$, there is a continuous phase transition at $K=1/q < 1$, as discussed above. The computations of $S = \omega - \xi\phi$ and μ is straight forward. We find

$$S(\phi) = \phi \ln(q/e) - (2/q)(1 - q\phi/2) \ln(1 - q\phi/2), \quad (6.12)$$

$$\mu(\phi) = (q/e)(1 - q\phi/2)^{1-2/q\phi}.$$

It should be noted that $S(\phi) \neq \tilde{S}(\tilde{E})$, even though the free energy $\omega = S + \xi\phi = \tilde{S} - \beta\tilde{E}$. Indeed, it is easy to see from (6.9) that

$$\tilde{S}(\tilde{E}) = -(2/q) \ln(1 - q\phi/2).$$

Thus the polymer picture gives rise to the entropy function $S(\phi)$, which is not identical to the entropy $\tilde{S}(\tilde{E})$ of the original spin model.

We now use the polymer picture to discuss the behavior of the system. The entropy is an analytic and convex function, and $\mu(\phi)$ is a decreasing function of ϕ . Hence the phase transition must occur only at $\phi=0$ or at $\phi=\phi_{\max}$. As we will see below, the transition occurs at $\phi=0$. Near $\phi=0$,

$$\begin{aligned} S(\phi) &\sim \phi \ln(1 - q\phi/2), \\ \mu(\phi) &\sim qe^{-q\phi/2}. \end{aligned} \quad (6.13)$$

Therefore $S(0)=0$, $\mu(0)=q$. Furthermore, $S'(0)=\ln q$; therefore the transition occurs only at $K=1/q$, as we saw above using the spin language. The maximum value of ϕ is given by $\phi_{\max} = 2/q$ and occurs as $K \rightarrow \infty$ [see (6.11)]. At ϕ_{\max} , $S(\phi_{\max}) = (2/q) \ln(q/e)$ and $\mu(\phi_{\max}) = (q/e)$. Thus $\mu(\phi)$ decreases by a factor of e as ϕ changes from 0 to ϕ_{\max} .

The maximum entropy occurs at $K=1$, at which ϕ takes the value $2(q-1)/q^2$. The maximum entropy is, therefore,

$$S_{\max} = S(\phi_{\max}) + 2/q^2.$$

The slope diverges to $-\infty$ as $\phi \rightarrow \phi_{\max}$ and therefore there is no transition at $\phi = \phi_{\max}$. All these conclusions are consistent with those derived from the spin language. Thus the diagram picture and the spin picture are equivalent. It can be shown that this remains true even when $H \neq 0$.

VII. SELF-AVOIDING SURFACES

A model of a self-avoiding surface has been identified as an $n = 0$ limit of a gauge model [15]. Again, we will be interested in the limit of a vanishing magnetic field of the gauge model. This limit corresponds to considering only closed self-avoiding surfaces. The self-avoiding constraint ensures that no more than two occupied plaquettes meet at a given bond of the lattice. Let N denote the total number of plaquettes and q the number of distinct plaquettes at each bond. The number of edges in the lattice is given by $4N/q$, since each plaquette has four bonds. The free energy per plaquette of the gauge model in the mean-field approximation is given by [15]

$$\omega = -3KM^4 + (4/q)\ln(1 + \frac{1}{2}K^2q^2M^6), \tag{7.1}$$

where M is the ‘‘spontaneous magnetization’’ per spin. The first term in (7.1) denotes the energy $-\beta\bar{E}$ and the second term represents the entropy $\tilde{S}(\bar{E})$ of the spin model, as was the case in the previous section. Again, the entropy $S(\phi)$ of the surface model, which will be calculated below, is not identical to $\tilde{S}(\bar{E})$ of the corresponding spin model.

Let us consider the spin model. The equilibrium value of M is obtained by maximizing ω : $\partial\omega/\partial M = 0$. This yields $M = 0$ as one of the solutions. The other solutions are given by

$$x = 1 + x^3/2k, \tag{7.2}$$

where

$$x = kM^2 > 0, \quad k = Kq > 0. \tag{7.3}$$

We have arbitrarily chosen $M \geq 0$ since we take $H \rightarrow 0+$. The first solution corresponds to

$$x = 0, \tag{7.4}$$

and yields $\omega = 0$. There are either no real solutions or two positive solutions of (7.2). Only the larger of the two yields a physical solution. The other solution does not maximize the free energy. The phase transition occurs at some $K = K_0$ at which the free energy of the new solution equals the free energy $\omega = 0$ of the $x = 0$ solution. As we will see, the transition is first order.

Let us now turn to the surface picture. Since $\partial\omega/\partial M = 0$ for the equilibrium solution, we have

$$\phi = K \frac{\partial\omega}{\partial K} = KM^4 = \frac{x^2}{Kq^2}. \tag{7.5}$$

For $x = 0$, we have $\phi = 0$ and $\omega = 0$ as said above. The entropy is also zero. For solutions of (7.2) we have

$$x = 1/(1 - q\phi/2). \tag{7.6}$$

Evidently, $x > 1$, i.e., $\phi > 0$. For these solutions, we can

reexpress ω in terms of ϕ . We get

$$\omega = -3\phi + (2/q)\ln Kq^2\phi = -3\phi - (4/q)\ln(1 - q\phi/2), \tag{7.7}$$

with ϕ given by

$$Kq^2\phi(1 - q\phi/2)^2 = 1. \tag{7.8}$$

We can now evaluate $S(\phi) = \omega - \phi\xi = \omega - \phi \ln K$:

$$S(\phi) = \phi \ln \left[\frac{q^2}{e^3} \phi(1 - q\phi/2)^{-2(2/q\phi - 1)} \right], \tag{7.9}$$

from which we obtain

$$\mu(\phi) = \frac{q^2}{e^3} \phi(1 - q\phi/2)^{-2(2/q\phi - 1)}, \tag{7.10}$$

for ϕ given by the solutions of (7.8). Near $\phi = 0$, $\mu(\phi) \cong (q^2/e)\phi e^{-q/\phi}$. Therefore $\mu = 0$ at $\phi = 0$ and rises, thus violating Theorem 4. The physical solution cannot correspond to the region where this theorem is violated.

Let us carefully investigate the problem. The maximum allowed ϕ is $\phi_{\max} = 2/q$. This situation corresponds to $x \rightarrow \infty$ [see (7.6)]. From (7.2), this happens when $K \rightarrow \infty$. From (7.10), we have $\mu \rightarrow 2q/e^3$ as $\phi \rightarrow 2/q$. Therefore $S(\phi) \rightarrow (2/q)\ln(2q/e^3)$ as $\phi \rightarrow \phi_{\max}$ and is non-

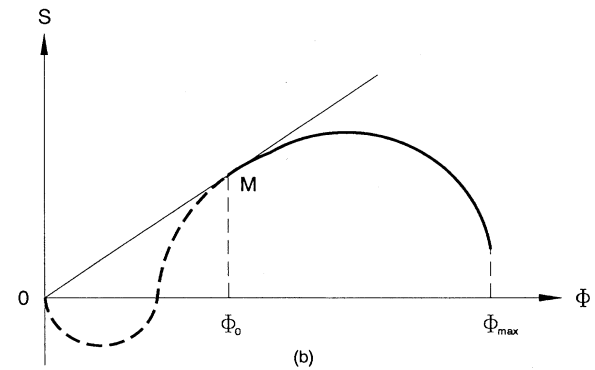
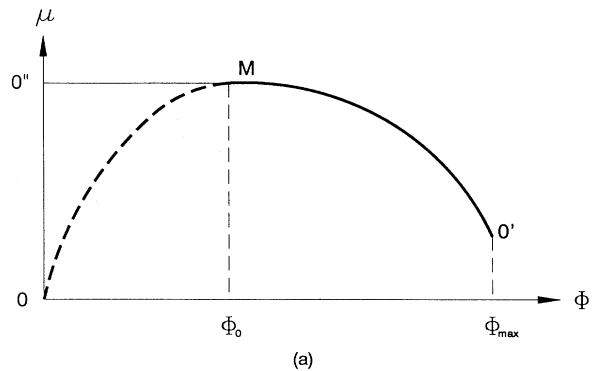


FIG. 6. (a) Growth function OMO' violating nonincreasing condition over the broken line segment OM and (b) corresponding entropy function violating convexity over the broken segment OM .

negative provided $q > e^3/2$. For $q < e^3/2$, the entropy must be set equal to zero as the mean-field approximation becomes highly inaccurate.

Let us evaluate $\mu'(\phi)$:

$$\mu'/\mu = 3/\phi + (4/q\phi^2)\ln(1 - q\phi/2).$$

We observe that $\mu' > 0$ whenever $\omega < 0$; see (3.21). Hence the region over which $\mu' > 0$, i.e., the region over which Theorem 4 is violated, also violates Theorem 2. In other words, the range $(0, \phi_0)$ over which $\mu' > 0$ [see Fig. 6(a)], is also where $\omega \leq 0$.

At some $\phi = \phi_0$, $\omega = \mu' = 0$. This determines ϕ_0 :

$$\ln(1 - q\phi_0/2) + \frac{3}{4}q\phi_0 = 0.$$

The phases with $\phi = 0$ and $\phi = \phi_0$ are in thermodynamic equilibrium as they have identical free energies. The entropy $S(\phi)$ must qualitatively appear as in Fig. 6(b). The tangent at ϕ_0 must pass through the origin since $\omega(\phi_0) = 0$. Thus there is a first-order transition from $\phi = 0$ to $\phi = \phi_0$ at some $K = K_0$ such that $S'(\phi_0) = -\ln K_0$. Furthermore, the equilibrium form of μ must be such that $\mu' = 0$ over the range $(0, \phi_0)$. This form is shown by the solid line in Fig. 6(a). This choice corresponds to the convex hull formed in Fig. 6(b).

It is evident that $\phi_0 < \phi_m$ [Fig. 6(b)], so that $K_0 < 1$. The solution of (7.8) valid over (ϕ_0, ϕ_{\max}) is given by

$$\phi_0 = (1/q)[1 + \sqrt{1 - 2/k}].$$

Thus $\phi_m = (1/q)[1 + \sqrt{1 - 2/q}]$ and $\phi_{\max} = 2/q$.

VIII. THE AXIS MODEL

The axis model, described below, is interesting because it exhibits both first-order and second-order transitions as the parameter n , the number of components of spins \mathbf{S} , is varied [32,33]. In the axis model, the spins, which are located at each site of the lattice, point along the $2n$ axes of the n -dimensional spin space:

$$\mathbf{S}: \{(0, 0, \dots, \pm\sqrt{n}, 0, \dots, 0)\}. \quad (8.1)$$

The only nonzero component is in the j th place where $j = 1, 2, \dots, n$. Hence there are $2n$ different orientations. Only nearest-neighbor spins interact via a ferromagnetic coupling $K = \beta J > 0$. The external magnetic field $\mathbf{H} = (H/\sqrt{n})(1, 1, \dots, 1)$ couples to each spin. The reduced Hamiltonian of the model is given by

$$\mathcal{H}_n = K \sum_{\langle i, j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j + \mathbf{H} \cdot \sum_i \mathbf{S}_i, \quad (8.2)$$

where $\langle ij \rangle$ denotes various nearest-neighbor pairs and i denotes various sites.

There is a diagrammatic expansion of the model in terms of "branched polymers" with multiple bonds, as shown in Ref. [14]. The partition function for the model (8.2) can be related to the following partition function:

$$Z = \sum_{\Gamma} n^L \eta^{V_0} K^B S(\Gamma) \mathcal{W}(L, B, V_0), \quad (8.3)$$

where $\eta = \tanh H$, $S(\Gamma)$ is a symmetry number for the

configuration Γ , and V_0 denotes the number of odd vertices of valency 1, 3, 5, In the limit $\eta \rightarrow 0+$ ($H \rightarrow 0+$), odd vertices have a vanishing density. Therefore let us suppress V_0 above. If we introduce

$$\mathcal{W}(B) = \sum_L n^L \mathcal{W}(L, B), \quad (8.4)$$

where the sum is over all possible L consistent with a given B (and a vanishing density of odd vertices), we can rewrite (8.3) as follows:

$$Z = \sum_{(B)} K^B \mathcal{W}(B). \quad (8.5)$$

Note that, because of the presence of n^L in (8.4), $\mathcal{W}(B)$ is a weighted sum of the number of configurations.

The model can be solved in a mean-field approximation [14]. In this approximation, the model exhibits a transition at a nonzero K . For $n \leq 3$, the transition is second order and occurs at $K = K_c = 1/q$. For $n > 3$, the model exhibits a first-order transition at $K = K_0 < K_c = 1/q$. However, as we will see below, there is a spinodal singularity at $K = K_c$ in the case of a first-order transition. The spinodal singularity is a feature of the mean-field approximation.

The free energy ω_n per bond as $H \rightarrow 0+$ is given by

$$\omega_n = -Km^2 + (2/q)\ln \left[\frac{\cosh(Kqm\sqrt{n}) + n - 1}{n} \right], \quad (8.6)$$

with the spontaneous magnetization m given by the equation of state

$$m = \frac{\sqrt{n} \sinh(Kqm\sqrt{n})}{\cosh(Kqm\sqrt{n}) + n - 1}. \quad (8.7)$$

The above choice of ω_n corresponds to choosing $\nu = 1$ in Ref. [14], since the average magnetization must be along one of the n axes at $H = 0$. This is certainly the case for $n \geq 1$ which we consider below. The first term in (8.6) is $-\beta\bar{E}$ and the second term is $\bar{S}(\bar{E})$. This is the spin language picture. We now investigate the model using the polymer picture below.

We note that $m = 0$ is always a solution, for which $\omega_n = 0$. Hence, $\bar{S} = 0$.

Let us now turn to possible nonzero solutions of (8.7). Since

$$\phi = K(\partial\omega_n/\partial K) = Km^2, \quad (8.8)$$

we have

$$\omega_n = -\phi + (2/q)\ln[C(y)], \quad (8.9)$$

where

$$y = Kqm\sqrt{n}, \quad (8.10)$$

$$C(y) = [\cosh y + n - 1]/n.$$

We can express ϕ in terms of y alone:

$$\phi = y \sinh(y)/nqC(y). \quad (8.11)$$

Since $\partial\phi/\partial y > 0$ for all $y > 0$, ϕ is a monotone nonde-

creasing function of y provided n is finite. In particular, near $y=0$,

$$\phi \sim y^2/nq. \quad (8.12)$$

Comparing (8.9) with $\omega_n = \phi \ln[K\mu(\phi)]$, we easily deduce that

$$\mu(\phi) = \frac{1}{eK} [C(y)]^{2/q\phi},$$

where K can be expressed in terms of y by the use of (8.7):

$$K = yC(y)/q \sinh(y) \equiv f(y), \quad (8.13)$$

which introduces $f(y)$ defined by the quantity in the middle. Finally, we get

$$\mu(\phi) = \frac{q \sinh y}{ey} [C(y)]^{2/q\phi-1}, \quad (8.14)$$

with ϕ given by (8.11).

Let us consider μ near $\phi=0$. From (8.12) we have

$$\mu(\phi) \sim q \exp[q\phi(n-3)/6]. \quad (8.15)$$

For $n > 3$, μ is a decreasing function at least near $\phi=0$. Indeed, it can be easily checked that $\mu(\phi)$ is a monotone decreasing function for $n \leq 3$.

For $n < 3$, the situation is different. We note from (8.15) that $\mu(\phi)$ is initially increasing, in direct violation of Theorem 4. Indeed $\mu(\phi)$ possesses a maximum at some $\phi=\phi_0$, as shown schematically in Fig. 6(a). According to the arguments given earlier in Sec. VII, we conclude that the rising branch of μ is unphysical. The physical branch is obtained from the convex hull of the entropy function and is given by the broken line of zero slope shown in Fig. 6(a). At the first-order transition at $K=K_0$, ϕ jumps from $\phi=0$ to $\phi=\phi_0$. At the transition, $\omega_n=0$. The transition point K_0 is given by (4.8), with $\mu(0)$ replaced by $\mu(\phi_0)$, since $\mu(\phi_0)$ is the value of the convex hull at $\phi=0$. Since $\mu(\phi_0) > \mu(0) = q$, K_0 is strictly less than $K_c = 1/q$.

The meaning of $K_c = 1/q$ can be deduced as follows. Consider (8.13), which we rewrite as follows:

$$y/Kq = f(y) = n \sinh(y)/C(y).$$

It is easy to see that $f'(0)=1$ and $f''(0)<0$. Therefore $f(y)$ crosses the straight line y/Kq an even number of times for $Kq > 1$, but an odd number of times for $Kq < 1$. Therefore, at $Kq=1$, i.e., at $K=K_c=1/q$, two of the crossings merge into one. In other words, $K=K_c$ is a spinodal point given by

$$K_c = 1/\mu(0). \quad (8.16)$$

The entropy function $S(\phi)$ is given by

$$S(\phi) = (2/q - \phi) \ln C(y) + \phi \ln(q/e) + \phi \ln \frac{\sinh y}{y}. \quad (8.17)$$

Near $\phi=0$, we find that

$$S = (n-3)q\phi^2/6 + \phi \ln q,$$

which has $\partial^2 S / \partial \phi^2 > 0$ for $n > 3$, implying that the convexity condition on S is violated. This violation implies a

first-order transition as discussed above. At the transition, the straight line through the origin touches S at $\phi=\phi_0$; the slope of the line gives $K=K_0$.

For $n=3$, we have a tricritical point at $\phi=0$.

Note that $y \rightarrow \infty$ as $K \rightarrow \infty$; see (8.13). Hence $\phi \rightarrow \infty$ as $K \rightarrow \infty$; see (8.11). This is because of multiple bonds in the diagrammatic expansion as discussed at the beginning of the section. Most importantly, each multiple bond of multiplicity σ contributes a symmetry factor $1/\sigma!$; see (8.3). This eventually forces $\mu \rightarrow 0$ or $S \rightarrow -\infty$ as $\phi \rightarrow \infty$.

IX. BRANCHED POLYMERS

In previous examples, the free energies of the models were known. Therefore extracting the entropy function $S(\phi)$ was straightforward. As it happens sometimes, the free energy is not easy to find. Rather, one only has the equation of state. This is the case, for example, when a model is solved on a Bethe lattice. In this case, one calculates the equation of state in a self-consistent manner, but the free energy cannot be evaluated. The last two examples that we consider here correspond to this situation. Only the equation of state is known and we wish to determine $S(\phi)$ in order to establish phase transitions. Note that one must compare free energies in different phases, since the free energy must be continuous at the transition. As we will demonstrate, the determination of the free energy from the equation of state is not always trivial and care must be exercised in the evaluation.

Our first example is of a model of branched polymers containing at most trifunctional branches. Let K , H , and w denote the activities of a bond, an end point, and a trifunctional branch, respectively. No loops are allowed. From (2.3) and (2.4), we observe that B , V_1 , and V_3 are the only independent quantities characterizing a configuration. In other words, P is no longer independent. Thus the partition function is given by (2.5) with $\pi=1$:

$$Z_N = \sum \Omega_N(B, V_1, V_3) K^B H^{V_1} w^{V_3}, \quad (9.1)$$

where the sum is over all possible values of B , V_1 , and V_3 on a finite lattice of size N . The polymers are self-avoiding.

Since $V_1 - V_3 = 2P$, we can rewrite (9.1) as follows:

$$Z_N = \sum \Omega_N(P, B, V_1) (H^2)^P K^B (wH)^{V_1}. \quad (9.2)$$

This form is suitable in the study of the dilute limit $\phi_p \rightarrow 0$ and corresponds to a zero density of polymers. From (9.2), it is evident that the limit is obtained by considering

$$\pi = H^2 \rightarrow 0, \quad (9.3)$$

keeping $wH = w'$ fixed and finite. As we will see below, the dilute limit turns out to be very singular.

The model (9.1) has been studied [25] on a Bethe lattice of coordination number $q=3$, by relating the partition function Z_N , $N \rightarrow \infty$, to that of an Ising model which includes two-body and three-body interactions along with an external magnetic field. The identification results in the following equation of state:

$$\sqrt{K}x^3 + (2H - wK)x^2 + (1 - 2K)x / \sqrt{K} = H, \quad (9.4)$$

where

$$x = \exp(2H') \geq 0,$$

with H' denoting the self-consistent field experienced by each Ising spin in the self-consistent solution. Because of the physical nature of the effective field H' , negative values of x are not allowed. The magnetization m of the Ising model is given by

$$m = (x - 1)/(x + 1).$$

Since $-1 \leq m \leq 1$, we have $x \rightarrow 0$ for $m = -1$ and $x \rightarrow \infty$ for $m = 1$. Let h be the external magnetic field in the Ising model. Then the equation of state in the form $h = f(m)$ can be easily integrated to give the free energy $\omega = g(m) - hm$ up to a constant where $g'(m) = f(m)$. However, h of the Ising model is not identical to H in (9.1), and obtaining $h = f(m)$ from (9.4) is not trivial. Therefore we have to determine ω differently.

We now demonstrate the use of the diagrammatic expansion technique in the following.

Let us consider the limiting case $H \rightarrow 0$. In this limit (9.4) reduces to

$$\sqrt{K}x^3 - wKx^2 + (1 - 2K)x / \sqrt{K} = 0, \quad (9.5)$$

and has $x = 0$ as a possible solution. The remaining two solutions either form a complex pair or are real. At $K = \frac{1}{2}$, the smaller of the two real solutions merges with $x = 0$ [see (9.6) below], and becomes negative, hence unphysical, for $K > K_c = \frac{1}{2}$. Thus K_c also represents a spinodal point. At $K = K'_c$, to be determined below, the above two real solutions annihilate each other. For $K < K'_c$, they form a complex pair. Hence, for $K < K'_c$, $x = 0$ is the only solution.

It appears from the above discussion that a phase transition must occur at some intermediate $K = K_0$ lying between K'_c and K_c . To locate K_0 requires calculating the free energies or, equivalently, the entropies for various solutions. We will, therefore, calculate the entropy function $S(\phi)$ below.

For $K > K'_c$, the two additional solutions of (9.5) are given by

$$x_{1,2} = \frac{1}{2\sqrt{K}} [wK \pm \sqrt{w^2K^2 - 4(1 - 2K)}]. \quad (9.6)$$

The two solutions merge at K'_c given by

$$K_c'^2 / (1 - 2K_c') = 4/w^2. \quad (9.7)$$

For $w \rightarrow 0+$, $K'_c \rightarrow \frac{1}{2} = K_c$. For $w \rightarrow \infty$, $K'_c \rightarrow 0$. At K'_c ,

$$x_1 = x_2 = x'_c = w\sqrt{K'_c}/2.$$

At $K = K_c$,

$$x_1 = x_c = w\sqrt{K_c}, \quad x_2 = 0.$$

The first-order phase transition at $H = 0$ survives even when $H > 0$. For some large $H = H_c$, the first-order transition terminates in a critical point in the H - K plane for a

fixed w . For $H > H_c$, there is no phase transition. For details, see Ref. [25].

We now proceed with the calculation of the entropy. We will no longer restrict ourselves to only $H = 0$. For arbitrary K , H , and w , the corresponding densities are given by

$$\begin{aligned} \phi &= y^2 / (K + y^2), \\ \phi_1 &= 2Hy^2 / (K + y^2) Q_0, \\ \phi_3 &= 2Wy^4 / 3(K + y^2) Q_0; \end{aligned} \quad (9.8)$$

see Ref. [25] for details. (The densities here are normalized by the total number of bonds, rather than the total number of sites as was the case in Ref. 25. Thus, densities in (9.8) differ from those in Ref. [25] by a factor of $\frac{3}{2}$.) The function Q_0 is given by

$$Q_0(y) = H + 2y + wy^2, \quad (9.9)$$

and

$$y = \sqrt{K}x. \quad (9.10)$$

To determine the entropy, we must express the activities K , H , and w in terms of densities ϕ, ϕ_1, ϕ_3 and use (3.16) and integrate to obtain S . Here the chemical potentials ζ_i are $\ln K$, $\ln H$, and $\ln w$, with corresponding densities ϕ, ϕ_1 , and ϕ_3 , respectively. We first observe from (9.8) that

$$y^2 = \frac{K\phi}{1 - \phi}, \quad (9.11)$$

and that

$$\phi_1 = 2H\phi / Q_0, \quad \phi_3 = 2wy^2\phi / 3Q_0. \quad (9.12)$$

Expressing H and w in terms of $\psi_1 = \phi_1/\phi$ and $\psi_3 = \phi_3/\phi$ from (9.12) into (9.9), we find that

$$2y / Q_0 = 1 - \frac{1}{2}(\psi_1 + 3\psi_3). \quad (9.13)$$

The equation of state (9.4) is written in a more convenient form

$$K = yQ_1 / Q_0, \quad (9.14)$$

where

$$Q_1 = 1 + 2Hy + y^2. \quad (9.15)$$

Reexpressing H in terms of ψ_1 from (9.12) and using (9.13), we find, after some algebra,

$$\ln K = \ln(1 - \phi) - \ln \phi + \ln A - \ln B,$$

where

$$A = 2\phi - \phi_1 - 3\phi_3,$$

$$B = 4 - 6\phi - 3\phi_1 + 3\phi_3.$$

Similarly, we find that

$$\ln H = \ln 2\phi_1 - \frac{1}{2} \ln A - \frac{1}{2} \ln B,$$

$$\ln w = \ln 6\phi_3 - \frac{3}{2} \ln A + \frac{1}{2} \ln B.$$

Incidentally, we note in passing that

$$Q_0/y = 4\phi/A, \quad Q_1 = 4(1-\phi)/B.$$

Integrating

$$\partial S / \partial \phi = -\ln K,$$

$$\partial S / \partial \phi_1 = -\ln H,$$

$$\partial S / \partial \phi_3 = -\ln w,$$

we find that

$$S = S_0 + \phi \ln \phi + (1-\phi) \ln(1-\phi) - \phi_1 \ln 2\phi_1 \\ - \phi_3 \ln 6\phi_3 - \frac{1}{2} A \ln A - \frac{1}{6} B \ln B,$$

where S_0 is a constant of integration that must be chosen so that $S=0$ in vacuum: $\phi = \phi_1 = \phi_3 = 0$. This yields $S_0 = \frac{2}{3} \ln 4$.

Now, the determination of the free energy is trivial. Using $\zeta\phi = \phi \ln K + \phi_1 \ln H + \phi_3 \ln w$ in (3.14), we find that

$$\omega = \ln(1-\phi) / (1-3\phi/2 - \phi_1/4 + 3\phi_3/4)^{2/3}. \quad (9.16)$$

It is easy to see that ω can also be written [34] as

$$\omega = \frac{2}{3} \ln [Q_1 / \sqrt{1+x^2}], \quad (9.17)$$

where Q_1 is given in (9.15). From (9.15) and (9.17), we observe that ω does not depend on w explicitly. However, it does depend on w implicitly since x depends on w (and other activities). The explicit dependence on various densities is given in the equivalent expression (9.16).

With the knowledge of S and ω , the entire thermodynamics of the system can be studied. Here, we will focus only on $H \rightarrow 0$. From (9.14), we find that

$$K = y(1+y^2)/(2y+wy^2).$$

Therefore, either $y=0$ or $y>0$. For nonzero y , K is given by

$$K = (1+y^2)/(2+wy) \quad (9.18)$$

and corresponds to a nonzero K for any $y>0$, provided w is finite. Thus, for very small K , $y=0$ is the only solution for which the free energy ω must be identically zero; see (9.17). Therefore, at the transition at some K , ω must also be zero. This $K=K_0$ is given by (9.17)

$$Q_1 = 1 + Kx^2 = \sqrt{1+x^2}.$$

For nonzero x , this gives us

$$x^2 = (1-2K)/K^2, \quad (9.19)$$

i.e.,

$$K = 1/(2+y^2). \quad (9.20)$$

Equating the two K 's given in (9.18) and (9.20), we find that at the transition $y=y_0$ is given by

$$(2+wy_0) = (1+y_0^2)(2+y_0^2). \quad (9.21)$$

For $w>0$, $y_0>0$. Thus, there is a first-order transition at $K=K_0$, from $y=0$ to $y=y_0$, with

$$y_0^2 = (1-2K_0)/K_0 \quad (9.22)$$

from (9.19). Obviously, $K_0 < \frac{1}{2}$ for $w>0$.

For $w \rightarrow 0$, there are no trifunctional branches ($\phi_3=0$). Hence we must recover the solution for linear polymers. From (9.21), we observe that $y_0=0$ at the transition. Hence the transition is continuous. Moreover, at the transition, $K_0 = \frac{1}{2}$ from (9.22). This is consistent with our discussion of linear polymers (SAW's) in Sec. VI.

For w very small, we can estimate K_0 and y_0 . Since y_0 is also small, we find from (9.21) that

$$2 + 2wy_0 \cong 2 + 2y_0^2,$$

i.e.,

$$y_0 \cong \frac{2}{3}w, \quad w \rightarrow 0.$$

Since K_0 must also be close to $K_0 = \frac{1}{2}$ for $w=0$, we find from (9.22)

$$K_0 \cong \frac{1}{2} - w^2/9, \quad w \rightarrow 0.$$

For $w \rightarrow \infty$, we note from (9.21) that $y_0^3 \sim w$. Hence, $K_0 \sim 1/w^{2/3}$ and goes to zero.

Let us now compare the prediction of a first-order transition at $K=K_0$, $w>0$, with the behavior of S near the vacuum state. In the vacuum state, $y=0$. For simplicity, consider the behavior of S along ϕ . Near $\phi=0$, $S \sim \phi \ln 2$. Thus the slope of S is smaller than $-\ln K_0$ (see above) for $w>0$.

Near $\phi=0$, $S(\phi) \sim \zeta_c \phi$, with $\zeta_c = \ln 2$. Thus, $K_c = \frac{1}{2}$, which is also the point where the transition occurs for SAW's ($w=0$). Therefore $\mu(0) = 1/K_c$, showing that the spinodal point K_c is given by the inverse of $\mu(0)$; see (8.16).

The study of the dilute limit corresponds to studying $H \rightarrow 0$, $w \rightarrow \infty$ [see (9.3)]. It should be evident from (9.4) that this limit is not different from $w \rightarrow \infty$ considered above. Hence we conclude that the dilute limit on the Bethe lattice is very singular, as claimed earlier, and gives rise to a first-order transition at $K_0 \rightarrow 0$ [35].

X. SELF-AVOIDING MANIFOLDS

As a final example, we consider a model of self-avoiding manifolds discussed in Ref. [10]. The model is solved recursively on a Bethe simplex lattice of coordination 3 described there. As usual, we obtain only the equation of state and not the free energy. The model for the manifolds is described by the partition function (2.11) and we are interested here in the limit $H \rightarrow 0$.

In the limit $H \rightarrow 0$, the equation of state is given by

$$K^{1/3}x^2(x^3-2) + x/K^{1/3} = 0, \quad (10.1)$$

where the elementary unit density ϕ for the manifolds is related to x via

$$\phi = x^3/(1+x^3), \quad (10.2)$$

as shown in Ref. [10]. Hence,

$$x^3 = \phi/(1-\phi). \quad (10.3)$$

In terms of ϕ , (10.1) can be rewritten as

$$K = \phi(1-\phi)^2 / [\phi(2-3\phi)]^{3/2} .$$

Therefore

$$S'(\phi) = -\ln K = -2 \ln(1-\phi) + \frac{1}{2} \ln \phi + \frac{3}{2} \ln(2-3\phi) .$$

Integrating, we obtain

$$S(\phi) = S_0 + 2(1-\phi) \ln[(1-\phi)] + \frac{1}{2} \phi \ln(\phi) - \frac{1}{2} (2-3\phi) \ln[(2-3\phi)] ,$$

where the constant S_0 of integration is determined by the condition $S(\phi=0)=0$. This yields $S_0 = \ln 2$. Finally, we have

$$S(\phi) = \ln \left[\frac{2\phi^{1/2}(1-\phi)^{2(1-\phi)}}{(2-3\phi)^{1-3\phi/2}} \right] , \quad (10.4)$$

and

$$\mu(\phi) = 8\phi^{1/2}(1-\phi)^{2(1/\phi-1)} / (1-3\phi/2)^{1/\phi-3/2} . \quad (10.5)$$

Near $\phi=0$,

$$\mu \approx 8 \left[\frac{\phi}{e} \right]^{1/2} e^{-\phi/4} .$$

Since $\mu'(0)$ is not negative, it violates our Theorem 4. As was the case in the previous section, this gives rise to a first-order phase transition.

Since $\mu(0)=0$, the spinodal singularity occurs at $K_c \rightarrow \infty$. That this is, indeed, the case can be seen as follows. For large enough K , there are three real and positive solutions of (10.1). The spinodal occurs when the middle root merges with the one at the origin. This occurs only when $K \rightarrow \infty$. Thus we note that the spinodal singularity is again determined by $\mu(0)$, i.e., by (8.16).

The free energy is easily calculated. We have

$$\omega = S + \phi \ln K = \ln \left[\frac{2(1-\phi)^2}{2-3\phi} \right] . \quad (10.6)$$

If we introduce

$$Q_1(y) = 1 + 2Hy^2 + y^4 , \quad (10.7)$$

where

$$y = K^{1/6} x , \quad (10.8)$$

we can rewrite (10.6) for $H=0$ as [34]

$$\omega = \ln [Q_1(y)/(1+x^3)] . \quad (10.9)$$

In fact, the free energy for $H>0$ is also given by (10.9), with y or x determined by the equation of state (see Ref. [10])

$$y = K^{2/3} Q_0 / Q_1 ,$$

when $Q_0 = H + 2y^2$. We will not pause here to show this.

We now turn back to the $H=0$ case and locate the transition point. Since for small enough K , $x=0$ is the only solution, the free energy is zero. Hence, at the phase transition, the free energy must remain zero. Therefore $Q_1 = 1 + x^3$. This yields $K^{2/3} x = 1$. From (10.1), we find

that $x=1$. Therefore at the transition $K=K_0=1$. The transition is from $x=0$ to $x=1$, i.e., from $\phi=0$ to $\phi=\phi_0=\frac{1}{2}$. The maximum possible value of ϕ is $\frac{2}{3}$ and corresponds to $x^3=2$; see (10.1) and (10.4). At $\phi=\phi_0$, $S(\phi_0)=0$. Moreover, $S(\phi_0)$ is maximum since $K=1$. Hence the transition is given by the slope of the tangent through the origin, i.e., by $K=1$.

The fact that $S(\phi)<0$ for all $\phi>\phi_0$ is due to the fact that we were considering self-avoiding manifolds on a $q=3$ coordinated Bethe simplex lattice. For large enough q , the entropy would be positive in the physically relevant range of ϕ . We can see this for self-avoiding surfaces considered in Sec. VII. From the discussion following (7.10), we know that the entropy at $\phi=\phi_{\max}$ is $(2/q)\ln(2q/e^3)$. Thus it is non-negative provided $q>e^3$. Thus, for $q=3$, this entropy is negative. Indeed, from (7.10), it is easy to see that $\mu(\phi)<1$ for $\phi \leq \phi_{\max}$. Thus $S(\phi)$ is always negative for $q=3$. We must choose q large enough to obtain a non-negative entropy.

XI. DISCUSSION AND SUMMARY

We have considered a general model of diagrams which can be a grand canonical ensemble or a canonical ensemble containing a fixed number of diagrams. Therefore the results obtained here are also valid for a system containing a single diagram. For simplicity, no interaction between diagrams except excluded-volume effects is allowed. However, the discussion can be easily extended to incorporate interacting diagrams with other than excluded-volume interactions, without altering any of the results obtained here. Thus the results obtained are very general.

Our central result is the following. A thermodynamic system of diagrams obeys the usual thermodynamic principles. In particular, the free energy ω (without the conventional $-\beta=-1/T$) must be maximized in equilibrium. This is true whether the diagrams form a physical system by themselves, as was the case in Secs. V–VII, IX, and X, or appear as a consequence of some expansions as in Secs. VI–VIII. In some cases, diagrams appear in some unrealistic limit of an otherwise physical model, as in Secs. VI and VII. In these two models, the partition function of the diagrammatic system is identical with that of the original spin model in the unphysical limit. Therefore the free energy of the diagrammatic system and of the original spin model must be maximized even in the unphysical limit since the free energy of the corresponding diagram system must be maximized. This must remain true even in the dilute limit.

The arguments for ω maximization do not depend on the number of objects in the ensemble. Therefore the arguments are applicable to the single-object canonical ensemble as well, with the same conclusion. In other words, the corresponding single-object free energy must also be maximized.

A single-object system can also be identified as a derivative of the free energy of the grand canonical ensemble at $\pi=0$; see, for example (2.5) and (2.6). Since $Z_{N,R}$ in (2.5) reduced to unity for $\pi=0$, we notice that

$Z_{N,\mathcal{R}}$ in (2.6) is equal to the derivative of the logarithm of $Z_{N,\mathcal{R}}$ in (2.5) with respect to π , evaluated at $\pi=0$. The free energy corresponding to (2.6) must be maximized.

The above result, which is our most important result, has not been appreciated in the past, as is evident from various calculations in which the stability of the free energy has been violated. Failure to invoke the maximization principle leads to an incorrect phase diagram as has been discussed elsewhere [35]. We refer the reader to this reference and other references cited therein.

Given the equation of state for a geometrical model, we show explicitly, by various examples, how to calculate the entropy and, hence, the free energy. The knowledge of these functions is essential in locating phase transitions, especially when we are dealing with first-order transitions.

As a by-product, we have calculated the entropy and the free energy for a collection of branched polymers with given densities ϕ , ϕ_1 , and ϕ_3 on a Bethe lattice of coordination number 3. The method presented here can be extended to any Bethe lattice of coordination number q . Such a solution, then, can be thought of as a mean-field approximation for branched polymers on a regular lattice of coordination number q . This will be reported elsewhere [36]. Similarly, we have obtained the entropy

and the free energy of self-avoiding surfaces and manifolds. Again, these results can be extended to any coordination number q .

An important property of the growth function was discovered: It is a nonincreasing function. In particular, the behavior of μ allows first-order or second-order transitions. The situation is very simple if the transition occurs at $\phi=0$. In this case, the behavior of μ near the origin determines the nature of the transition.

(1) If μ is a constant over a finite range near the origin, the transition is first order in nature.

(2) If μ is decreasing near $\phi=0$, we have a continuous transition.

In mean field, it happens sometimes that μ is not a nonincreasing function. In this case, the branch over which μ is increasing is unphysical and must be replaced by a straight segment of zero slope. In this case, the value $\mu(0)$ of the original function at $\phi=0$ locates the spinodal point. The growth function, thus, is a useful quantity that provides us with important information about the behavior of the model.

In summary, we have demonstrated that the diagrammatic approach is an alternative important approach that, in some cases, may be very simple in order to understand the model of interest.

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