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Metastability and spinodals in the lattice gas model

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Abstract. The droplet model of condensation as developed by Fisher is modified to take account of: (*a*) *ramified* clusters whose surface/volume ratio tends to a finite limit as the number n of constituent molecules becomes large; (*b*) the excluded volume interactions between clusters. It is found that the interactions change the position of the first singularity in the activity series so that it no longer coincides with the phase boundary but is located beyond it. A thermodynamic metastable state can then be defined as in the classical Gibbs picture. At sufficiently low temperatures *compact* clusters (ie those in which the surface/volume ratio tends to zero for large n) dominate and give rise to an essential singularity. Near the critical temperature ramified clusters dominate and give rise to a spinodal line with a branch point singularity. Critical behaviour can be explained in terms of ramified clusters alone.

1. Introduction

During the 1930s two independent approaches were pursued for the problem of the condensation of a classical gas of molecules with short-range repulsive forces and longer-range attractive forces. The cluster integral theory developed by Mayer (and Ivon) following initial steps taken by Ursell, succeeded in obtaining formally a power series expansion for the free energy. When the expansion variable is the absolute activity, the coefficients are multiple integrals of the intermolecular potential termed 'cluster integrals'; when the expansion variable is the density, the coefficients are termed 'irreducible cluster integrals' and are simply and directly related to the virial coefficients of the condensing gas. The formalism can be developed elegantly using the concepts of graph theory (for a general review see Uhlenbeck and Ford 1962, Domb 1974, chap 1, § 3).

There were high hopes in the 1940s and early 1950s that this development would lead to a detailed description of the liquid–vapour phase transition, and the phenomena associated with the critical point. However, it became clear that the problem of assessing the behaviour of higher-order cluster integrals presented formidable difficulties, and little progress was made either theoretically or numerically.

A question discussed at some length in the earlier literature is the radii of convergence of the two power series, and their physical significance. It was first assumed that these radii of convergence would correspond to the phase boundary, and that the series might also contain a potential description of the liquid phase. The rigorous

treatment by Yang and Lee (1952) of a lattice gas provided strong evidence that this was not the case, and that to explain the equilibrium between the two phases, a second function must be defined which started from the liquid side (see e.g. Yang 1972). The alternative interpretation was then put forward that the radii of convergence might represent the limit of stability of the condensing gas, which, in accordance with the classical ideas of Gibbs, was taken to be beyond the equilibrium condensation point.

Subsequent detailed analysis of the lattice–gas model (Gaunt and Domb 1975) has shown that the density expansion is complex, and that its radius of convergence does not correspond to a physical singularity. The nature of this expansion changes from lattice to lattice, and the series is not suitable for asymptotic assessment. However, the activity series settled down to a regular pattern of behaviour which can be related to the critical point and its properties.

In parallel with the above development, a non-rigorous but empirical approach to the problem was initiated by Becker and Döring (1935) which considered the growth of individual droplets and applied the methods of chemical kinetics to estimate their growth. This approach was further explored by Bijl (1938), Frenkel (1939a, b) and Band (1939a, b), and Frenkel's treatment forms the basis of modern nucleation theory (Zettlemoyer 1969). Each droplet is treated as a sphere whose free energy depends on its surface and volume and is therefore determined by its radius. No attempt is made to take account of interactions between droplets, and the possibility of different sizes and shapes of droplet are regarded as of secondary importance. In nucleation theory these assumptions are reasonable.

In fact, as indicated above, the cluster integral treatment makes no such assumptions and treats the problem correctly and exactly. However, Frenkel (1939a) argued with some cogency that the theory 'because of its mathematical intricacy will hardly appeal to the experimental physicist or chemist'.

The droplet approach was taken up in a preliminary way by Essam and Fisher (1963), and in more detail by Fisher (1967). By using the results of Ising model enumerations, Fisher was able to take account of the different sizes and shapes of droplet, and to conjecture a formula for the entropy of droplets in relation to their surface area. He then constructed a mimic partition function from which he drew a number of conclusions. Among them are: (*a*) the radius of convergence of the activity series is identical with the phase boundary below the critical temperature; (*b*) the activity series terminates in an essential singularity; (*c*) no metastable extension of the gaseous phase beyond the phase boundary exists in the true thermodynamic sense.

Fisher's treatment is unsatisfactory in two important respects; it ignores the effect of a wide class of droplets, and it fails to take the interaction between droplets into account. Attempts have been made to modify the treatment to remedy these defects (eg Reatto 1970, Reatto and Rastelli 1972, Stauffer *et al* 1971), but we feel that they are empirical in character and do not get to the heart of the problem. In the present paper, therefore, we return to the Mayer treatment in its application to the Ising or lattice-gas problem. We find that we can modify Fisher's treatment so as to include an 'interaction function' to take account of the volume exclusion of droplets. We also take account of an extensive class of 'ramified' droplets which were not considered by Fisher. In certain particular cases the interaction function can be calculated exactly, and more generally, series expansions can be developed from which its behaviour can be estimated. From this treatment we are led to conclusions, some of which differ substantially from those of Fisher; and in the neighbourhood of the critical point we find that ramified droplets play a dominant role.

2. Classical description of phase equilibrium

We first summarize the essential features of the classical theory of phase equilibrium as indicated by van der Waals equation and amplified by Gibbs. Figure 1 shows the standard form of isothermal below the critical temperature T_c. The stable equilibrium

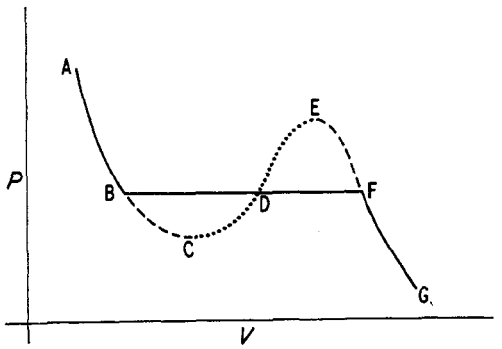

Figure 1. Stable and metastable states in the van der Waals picture. Points C and E are spinodals and represent the limits of stability of the liquid and gaseous phases. Full curve, stable; broken curve, metastable; dotted curve, unstable.

state corresponds to A B D F G, where the horizontal line B D F is drawn so as to make the areas B C D and D E F equal. However, if the vapour phase is suppressed, the liquid phase A B can be continued as a metastable extension as far as C where $(\partial p/\partial V)_T$ becomes zero. No extension is possible beyond C since the phase becomes thermodynamically unstable. Likewise, if the liquid phase is suppressed, the vapour phase can be continued as a metastable extension as far as E where it ceases to be stable. Points C and E trace out 'spinodal lines', and the phenomenon of spinodal decomposition is of great importance in the kinetics of phase growth (Cahn 1971).

The magnetic analogue of the above is illustrated in figure 2, where the magnetic field H corresponds to the pressure, and the magnetization to the density (N/V). However, there is a great simplification in the magnetic system because of the symmetry in regard to reversal of magnetic field. We shall therefore concentrate on the magnetic problem since it is widely felt that the patterns of behaviour for fluids and magnets are very similar (see eg Vicentini-Missoni 1972).

It is instructive to look at the above picture in terms of free energy. Figure 3 represents the Helmholtz free energy as a function of magnetization. The stable phase corresponds to the 'two-tangent' line B F, and the spinodal lines to points of inflection. Finally, figure 4 presents the more usual picture of the Gibbs free energy as a function of temperature, where the metastable extensions correspond to supercooled and superheated phases. It should be noted that the two phases are represented by separate analytic functions, and there is no singularity in either phase at the point of stable equilibrium. In this picture the spinodal lines correspond to points of infinite curvature in the (G, p) plane.

The above classical picture has been shown to follow rigorously from statistical mechanics for models with very long-range forces, ie of the form $\lambda J \exp(-\lambda R)$ where λ is allowed to tend to zero (Hemmer and Lebowitz 1975). The basic physical problem is

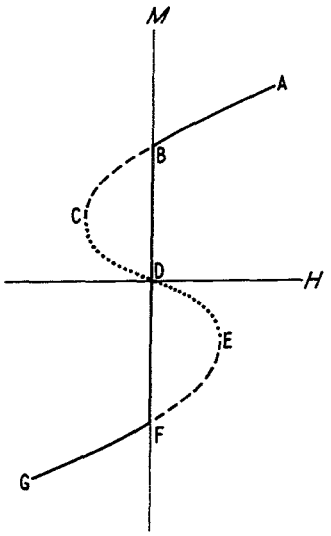

Figure 2. Stable and metastable states in the classical picture of a ferromagnet. Points C and E are spinodals and represent the limits of stability of spin-up and spin-down phases. Full curve, stable; broken curve, metastable; dotted curve, unstable.

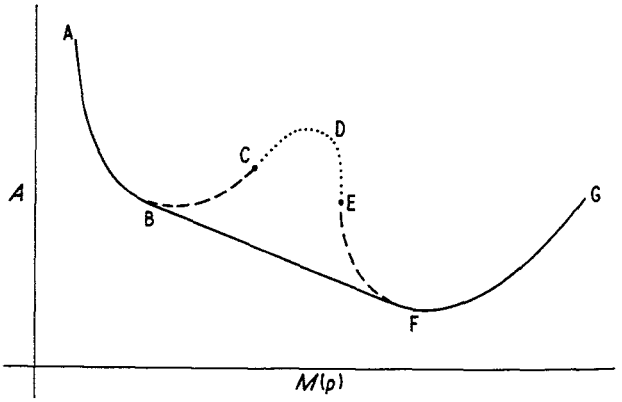

Figure 3. Helmholtz free energy of a classical ferromagnet (or fluid). Points of inflection C and E are spinodals which represent the limits of stability of the phases. Full curve, stable; broken curve, metastable; dotted curve, unstable.

to find how this picture is modified when realistic short-range forces are substituted for the long-range forces; these introduce surface effects which play a major role in determining the growth and interaction of finite clusters.

3. Metastable states in the Ising model

Consider an Ising model of N spins with nearest-neighbour interactions in a large magnetic field H at a given temperature T. If the field is sufficiently large the spins will

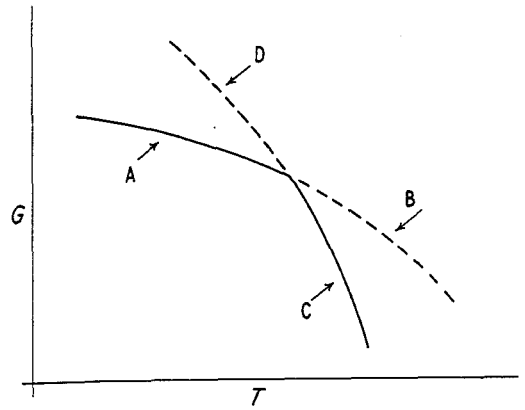

Figure 4. Gibbs free energy of a classical fluid (or ferromagnet). The two phases correspond to two different analytic branches and there is no singularity in either at their intersection. Full curve, stable; broken curve, metastable. A, phase I; B, phase I, superheated; C, phase II; D, phase II, superheated.

all line up in the direction of the field. We now gradually reduce the field H, allowing spins to overturn in accordance with Boltzmann's relation. However, to obtain a metastable state we must suppress the second phase, which consists of all the spins aligned in a direction opposite to the field and states derived from it, by overturning a finite number of spins. As long as $H > 0$ such states are excluded when N is large by the Boltzmann factor, which is of order $\exp(-N\beta mH)$ (where m is the magnetic moment of a spin). However, when $H \leqslant 0$ these states are of major importance in determining thermodynamic equilibrium, and our system is metastable.

Any excited state can now be characterized as a series of groups of overturned spins connected together as 'droplets' (figure 5). All sizes and shapes of droplet are possible, and there is an interaction between droplets arising from their finite size (excluded volume interaction). Each individual droplet, consisting of n connected overturned spins and s broken bonds, has a Boltzmann factor $y^n z^s$ where

$$y = \exp(-2\beta mH), \qquad z = \exp(-2\beta J) \tag{1}$$

and J is the energy of interaction of a pair of parallel spins. To ensure that the system

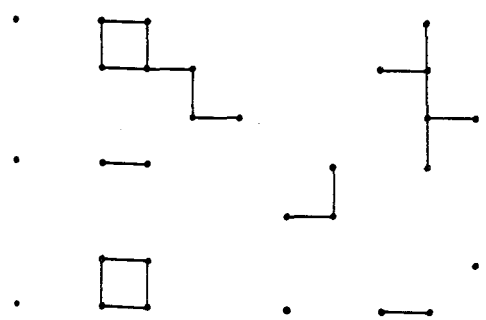

Figure 5. Interacting droplets in the Ising model.

remains metastable we must further restrict any droplet from growing to a size of order N (Penrose and Lebowitz 1975, unpublished).

In the lattice gas interpretation, each overturned spin corresponds to a particle, and the original spins correspond to holes.

Each droplet corresponds to an embedding of a connected graph of n vertices and l lines on the lattice, where the surface area of the droplet is defined by

$$s = nq - 2l \tag{2}$$

and q is the coordination number of the lattice. The number of embeddings of the graph on the lattice is usually referred to as the *strong lattice constant* of the graph (see eg Domb 1974). The term *strong* is used to describe embeddings in which all occupied sites which are nearest neighbours are connected by a bond of the graph. We shall denote the *total* number of strong embeddings of *all* connected graphs with a given n and l by $G(n, l)$, and this represents the total number of droplets of n spins with a given surface area s; it also defines the entropy of droplets with this surface area.

4. Specification of droplets

Following Fisher (1967), we now classify droplets according to their shape. For a given n there is a minimum possible value of s, say s_0, corresponding to the most compact embedding, and a maximum value s_1 ($= nq - 2n + 2$) corresponding to the embedding of Cayley tree configurations. As n becomes large s_0 corresponds to a sphere in three dimensions, or a circle in two dimensions. Fisher found it convenient to introduce a parameter σ to specify the shape, where

$$s \simeq An^{\sigma}, \qquad (\sigma_0 \leqslant \sigma \leqslant 1). \tag{3}$$

The constant A is a numerical factor of order unity, taking account, for example, of the difference between cubical or spherical droplets which have the same value of σ; the formula applies asymptotically for large n. σ_0 corresponds to the most compact embeddings, and is equal to $\frac{2}{3}$ in three dimensions and $\frac{1}{2}$ in two dimensions, $\sigma = 1$ corresponds to 'ramified' embeddings whose surface is proportional to their bulk.

It is possible to specify A precisely only for configurations of a particular shape. Since new shapes enter continually as n increases, it is better for some purposes to drop the constant A, and σ can then be uniquely defined for any configuration. The distribution $G(n, l)$ can be derived numerically for finite n and the change to σ represents a convenient change of scale. Our main interest is in the asymptotic behaviour of $G(n, l)$ for large n, and we shall assume that it approaches a continuous distribution $\Gamma(n, \sigma)\, d\sigma$, where $\sigma_0 \leqslant \sigma \leqslant 1$.

Fisher confined his attention to droplets with $\sigma_0 < 1$ which we shall call *compact* (figure 6(a)). This is the type of droplet envisaged in the earlier theories without any internal holes. However, he took an important step forward in estimating the entropy of such droplets as a function of s. In two dimensions the 'surface' of each droplet is a self-avoiding polygon whose length is approximately proportional to s. It has been well established by numerical studies that the number of such polygons $u(s)$ is asymptotically of the form (see eg Domb 1969)

$$u(s) \sim \mu^s / s^{\tau}. \tag{4}$$

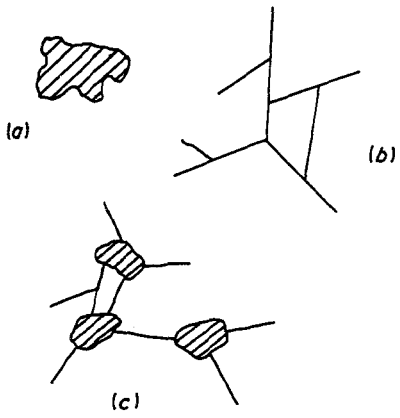

Figure 6. Different types of droplet: (*a*) compact, $\sigma < 1$; (*b*) ramified, $\sigma = 1$; (*c*) hybrid.

Here μ is a numerical constant characteristic of the lattice, and τ is an exponent which appears to be universal (ie independent of lattice structure) in a given dimension.

Fisher assumed that a formula of type (4) is valid quite generally for droplets of any particular σ in any dimension, and this suggestion seems very plausible. He further assumed that for large s one particular value of σ, say $\bar{\sigma}$, would dominate asymptotically over all others. This is again supported by numerical studies on self-avoiding polygons in two dimensions (Hiley and Sykes 1961), the appropriate value of $\bar{\sigma}$ then being $\frac{2}{3}$. The assumption means that for compact droplets the distribution $\Gamma(n, \sigma)$ approaches the form

$$\Gamma(n, \sigma) \sim \tilde{\mu}^{n^{\bar{\sigma}}} n^{-\bar{\sigma}\tau} \delta(\sigma - \bar{\sigma}). \tag{5}$$

We now take account of droplets with $\sigma = 1$ which were not considered by Fisher. We shall call these *ramified*; they include self-avoiding walks and polygons, and Cayley trees with a finite number of nodes, and are therefore very extensive; a typical ramified droplet is depicted in figure 6(*b*). It is clear that they are extensive in number, and must lead asymptotically to a term in $\Gamma(n, \sigma)$ of the form

$$\mu_0^n n^{-\tau_0} \delta(\sigma - 1). \tag{6}$$

Our first suggestion in a preliminary publication (Domb 1975) was to combine (5) and (6) in an attempt to represent the asymptotic behaviour of $\Gamma(n, \sigma)$. However, even a cursory glance at numerical data for finite n shows this to be unsatisfactory. We have ignored *hybrid* droplets (figure 6(*c*)) which fill in the values of σ between $\bar{\sigma}$ and 1. New types of hybrid droplet enter so extensively that they eliminate any trace of a maximum at $\sigma = \bar{\sigma}$. This will be seen from figure 7 where we have plotted the distribution of weak embeddings $g(n, l)/w(n)$ as a function of l/n for the face-centred cubic lattice with $n = 6$ and 7. Data are taken from the tables of Baker *et al* (1967), and

$$w(n) = \sum_l g(n, l) \tag{7}$$

is the total number of weak lattice constants of graphs with n points†. (Weak lattice constants are embeddings with no restrictions about nearest-neighbour occupation.) Although the data refer to weak rather than strong lattice constants, there are good

† The data for $n = 7$ are incomplete, but we believe that the general pattern represented is correct.

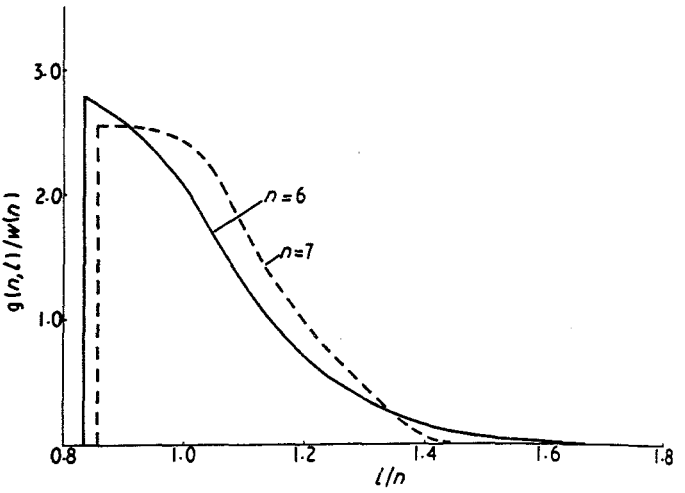

Figure 7. Distribution of weak lattice constants. The left-hand side corresponds to ramified configurations and the right-hand side to compact configurations. (Histogram plots have been transformed into a smooth curve.)

reasons for thinking that there is little difference in basic behaviour between the two sets. This is because strong embeddings are equivalent to weak embeddings on a lattice with no nearest-neighbour occupation; such a restriction increases the excluded volume of an occupied site but does not basically change the problem, if we accept current ideas on universality. In any case, we shall transform to a weak embedding expansion in § 6.

Fisher's treatment is based on the idea that droplets with $\sigma < 1$ play a fundamental role. At sufficiently low temperatures this should be correct, and we shall now discuss his treatment in more detail.

5. Partition function for non-interacting droplets

If we ignore the volume exclusion of droplets, which should be reasonable at sufficiently low temperatures where the densities are small, we can write down the partition function for the metastable system in the form

$$\ln Z(\beta, H) = \sum_{n,l} G(n, l) y^n z^s \qquad (s = nq - 2l). \tag{8}$$

Taking only compact droplets into account as in (5), Fisher (1967) was led to a 'mimic' partition function of the form

$$\ln Z(\beta, H) = \sum_{n} y^n z^{n^\sigma} \bar{\mu}^{n^\sigma} n^{-\bar{\sigma}\bar{\tau}}. \tag{9}$$

From this partition function he drew the following conclusions about the singularities of the system: (*a*) The power series in y always has radius of convergence 1; there is an essential singularity on the phase boundary ($H = 0$, $y = 1$) since all derivatives of $\ln Z$ converge at $y = 1$. (*b*) When $H = 0$ and $y = 1$ the power series in z has radius of convergence $\bar{\mu}^{-1}$ and this value corresponds to the critical temperature T_c.

(c) Critical exponents depend on two parameters $\bar{\sigma}$ and $\bar{\tau}$ which are related to the statistical geometry of compact droplets.

For the physicist who is unfamiliar with essential singularities and their properties we should like to offer the following interpretation. Consider a power series with a branch point singularity

$$F(x)=\sum x^n/n^g \sim (1-x)^{g-1} \qquad (g>2). \tag{10}$$

$F(x)$ and its first t derivatives will be finite, where t is the integral part of $(g-1)$. As g becomes very large we approach a situation in which nearly all derivatives are finite. In the limit of g becoming infinite and n^g being replaced by a^{n^σ} $(a>1)$ we obtain an essential singularity.

There are a number of criticisms of the mimic partition function (9) as a description of behaviour near the critical point. Gaunt and Baker (1970) pointed out that the partition function has a line of singularities on $y=1$ *above* the critical temperature, and in fact the function itself and all its derivatives are now infinite. This result is clearly incorrect since there are no singularities for $T>T_c$; one is therefore led to suspect the conclusions for T near T_c on the low temperature side. Also the terms in (9) do not satisfactorily mimic the low density expansions which have been calculated for standard lattices. For example, putting $y=1$, all the terms of (9) are positive for all lattices, whereas the actual term structure is very complex and lattice dependent. This aspect has been discussed in more detail by Domb and Guttmann (1970).

In addition, the numerical values of $\bar{\sigma}$ required to fit critical exponent values are surprising. In both two and three dimensions the estimates are close to σ_0 (in three dimensions the estimate is *below* σ_0 which is impossible geometrically as noted by Fisher); however, the statistical data on two-dimensional droplets (Hiley and Sykes 1961) would lead one to expect a value in the neighbourhood of $\frac{2}{3}$.

Let us now take into account ramified droplets with $\sigma=1$ introduced in the previous section. Using formula (6) to estimate their number we obtain a contribution to $\ln Z(\beta, H)$ of the form

$$\sum y^n z^{\bar{a}n} \mu_0^n n^{-\tau_0}, \tag{11}$$

where $\bar{a}$ refers to the type of droplet which dominates asymptotically. The function represented by (11) behaves very differently from (9). The radius of convergence of the y series is no longer $y=1$, but instead

$$y_c=(\mu_0 z^{\bar{a}})^{-1} \tag{12}$$

and this is greater than 1 at sufficiently low temperatures. The singularity in the y series is now a branch point of the type usually associated with critical behaviour, and it would lead us to expect a spinodal at y_c.

The singularities associated with (9) and (11) are shown schematically in figure 8, and we see that in this approximation Fisher was correct to ignore ramified configurations, since the dominant singularity in the y series is provided by compact configurations. However, from the general discussion given above we should expect the approximation of ignoring the volume exclusion of droplets to be valid only at low temperatures. We shall therefore try to reformulate the problem so as to take these interactions into account.

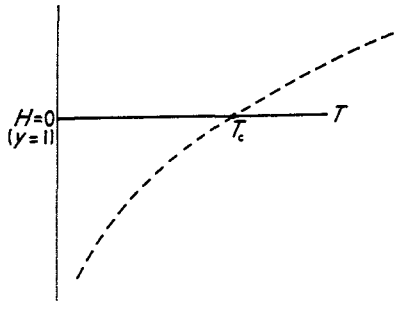

Figure 8. Singularities in Fisher's model (ignoring excluded volume). The full line represents essential singularities and the broken curve branch point singularities.

6. Mayer development for the Ising model

The Mayer formalism has been applied to the Ising model by a number of authors including Fuchs (1942), Yvon (1945, 1948), Rushbrooke and Scoins (1955) and Domb and Hiley (1962). (For a review see Domb 1974, chap 6.) The activity λ corresponds to yz^q, and the activity expansion can be written in the form

$$\ln Z = \sum_{r=1}^{\infty} \lambda^r F_r(z) \tag{13}$$

where $F_r(z)$ is a polynomial in z. Corresponding to the connected graph expansion for a continuum, we have a *connected lattice constant* expansion in which each contribution to $F_r(z)$ is associated with an embedding of a connected graph on the lattice. We then sum all contributions corresponding to a particular embedding, deriving an expansion of the form

$$\ln Z = \sum_{i,n} G_i(n, l)\Phi^{(i)}_{n,l}(y, z). \tag{14}$$

Here i refers to a particular type of graph with n points and l lines, $G_i(n, l)$ is its strong lattice constant, and $\Phi^{(i)}_{n,l}(y, z)$ is a function which can be calculated from partition functions of finite clusters.

To illustrate (14) we quote the functions $\Phi^{(i)}_{n,l}(y, z)$ for the first few connected graphs. For $n = 1$ the only graph consists of single point, •, and

$$\Phi_{1,0}(y, z) = \ln(1+\lambda) = \lambda - \tfrac{1}{2}\lambda^2 + \tfrac{1}{3}\lambda^3 \ldots (\lambda = yz^q). \tag{15}$$

For $n = 2$ the only graph consists of a single term with two points, •——•, and

$$\Phi_{2,1}(y, z) = \ln(1+2\lambda+\lambda^2 z^{-2}) - 2\ln(1+\lambda) = \lambda^2 z^{-2}(1 - z^2 - 2\lambda + 2\lambda z^2 + O(\lambda^2)). \tag{16}$$

For $n = 3$ there are two graphs  , and  and

$$\Phi_{3,2}(y, z) = \ln[1+3\lambda+\lambda^2(1+2z^{-2})+\lambda^3 z^{-4}] - 2\ln(1+2\lambda+\lambda^2 z^{-2}) + \ln(1+\lambda)$$
$$= \lambda^3 z^{-4}[(1-z^2)^2(1-4\lambda)+O(\lambda^2)] \tag{17}$$

$$\Phi_{3,3}(y, z) = \ln(1+3\lambda+3\lambda^2 z^{-2}+\lambda^3 z^{-6}) - 3\ln(1+2\lambda+\lambda^2 z^{-2}) + 3\ln(1+\lambda)$$
$$= \lambda^3 z^{-6}[(1-3z^4+2z^6) - 3\lambda(1+z^2-5z^4+3z^6)+O(\lambda^2)]. \tag{18}$$

These functions are calculated by the finite cluster method which has been used effectively for a number of problems, and which is described in detail elsewhere (Domb 1974, chap 6, § 2 B3).

To make contact with the approximation (8) of the previous section we note that the largest term in $\Phi^{(i)}_{n,l}(y, z)$ at sufficiently low temperatures is always $\lambda^n z^{-2l}$, which is equal to $y^n z^s$ in view of (2). We can therefore write

$$\ln Z = \sum_{i,n} G_i(n, l) y^n z^s \Psi^{(i)}_{n,l}(y, z) \tag{19}$$

where $\Psi^{(i)}_{n,l}$ represents the effect of interactions and is 1 at sufficiently low temperatures. We should stress however that when interactions are taken into account there is no longer any simple connection between the terms in (19) and the distribution of droplets of given size and shape. The factor $\Psi^{(i)}_{n,l}(y, z)$ contains contributions corresponding to all possible ways of making graphs with given (n, l) by overlapping graphs in pairs, triplets, etc with smaller (n, l). It is possible to calculate the distribution of droplets of given size and shape when interactions are taken into account. The calculations are very complex, and we do not feel that they have any direct association with critical behaviour. We shall return to this point later.

As with all expansions in terms of lattice constants, it is possible to transform from the strong to the weak system, and to write (19) in the form

$$\ln Z = \sum_{i,n} g_i(n, l) y^n z^s \psi^{(i)}_{n,l}(y, z). \tag{20}$$

There are several advantages of this formulation. The weak lattice constants enter naturally into high temperature expansions and are better known and tabulated; also it is possible to calculate the $\psi^{(i)}_{n,l}(y, z)$ powers of λ from cluster integrals, as is shown in the appendix. The values of $\psi^{(i)}_{n,l}(y,z)$ corresponding to the graphs above are identical with $\Psi^{(i)}_{n,l}(y, z)$ for the first three and differ only for the triangle for which

$$\psi_{3,3}(y, z) = (1-z^2)^3(1-3\lambda) + O(\lambda^2). \tag{21}$$

We now consider the evaluation of $\psi^{(i)}_{n,l}(y, z)$ in two limiting cases corresponding to $\sigma = 1$ and $\sigma = \sigma_0$. For Cayley trees an exact evaluation is possible by the finite cluster method; from it we deduce that

$$\psi^{(i)}_{n,l}(y, z) \sim [\psi_i(y, z)]^n \tag{22}$$

where the particular ψ_i denoted by ψ_R for convenience is given by

$$\psi_R = \frac{1}{\theta} \frac{(1+\theta) - [(1-\theta)^2 + 4\theta z^2]^{1/2}}{(1+\theta) + [(1-\theta)^2 + 4\theta z^2]^{1/2}} \qquad (\theta = yz^{q-2}). \tag{23}$$

If we expand (23) as a power series in θ we find that

$$\psi_R = (1-z^2)[1 - \theta z^2 + O(\theta^2)]. \tag{24}$$

For a compact configuration whose surface sites are small in number compared with the bulk sites, the method outlined in the appendix indicates that a relation of type (22) is again valid, and $\psi_i(y, z)$ (denoted by ψ_C) can be expanded as a series

$$\psi_C = (1-z^2)^{q/2}[1 - yz^q + O(y^2 z^{2q-2})]. \tag{25}$$

In fact, for any configuration with an asymptotically defined shape (22) is valid, and ψ_i will have a value lying between (24) and (25).

We shall now examine the consequences of the interaction on the distribution of singularities in the limiting cases $\sigma = 1$ and $\sigma = \sigma_0$.

7. Effect of excluded volume on the singularities

We shall start from the weak lattice constant expansion (20), but we refer to the terms as corresponding to compact or ramified *configurations* rather than droplets. Although compact configurations correspond rather loosely to compact droplets and ramified configurations to ramified droplets, there is a direct correspondence only in the limit of low density as mentioned above.

We first discuss the properties of the ramified Cayley tree configurations for which (22) is valid, the appropriate ψ_R being given by (23). Instead of (11) we now have for the contribution of these configurations,

$$\ln Z \text{ (ramified)} = \sum y^n z^{a'n} \psi_R^n \mu_0'^n n^{-\tau_0'}, \tag{26}$$

where the primes have been used to represent parameters corresponding to weak lattice constants. The function of y defined by (26) will have branch point singularities at values of y given by

$$y_c \psi_R(y_c, z) = (\mu_0' z^{a'})^{-1}, \tag{27}$$

instead of (12).

The curve of singularities defined by (27) has been discussed in detail by Domb and Guttmann (1970), who concluded that it is of the general form indicated in figure 9. The factor ψ_R lowers the curve of figure 8 so that it no longer crosses the axis and hence fits the requirements of the Yang–Lee theorem (1952). However, to assess the detailed behaviour in the neighbourhood of T_c, a more careful analysis of the contributions of different ramified configurations is required, and this has not yet been carried out.

Coming now to compact configurations we have seen that (22) is valid; we do not now have a closed form expression for ψ_C but an expansion (25) valid at low temperatures. Instead of (9) we have for the contribution of this type of configuration,

$$\ln Z \text{ (compact)} = \sum_n y^n \psi_C^n z^{n\sigma} \mu'^{n\sigma} n^{-\sigma\tau} \qquad (\sigma < 1). \tag{28}$$

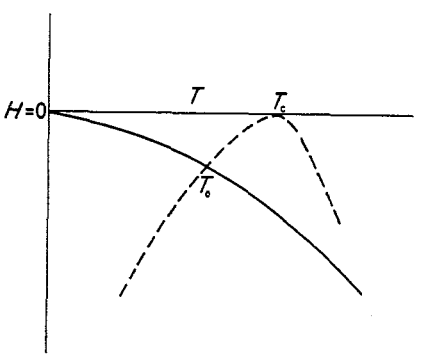

Figure 9. Singularities when excluded volume effects are taken into account. ... represents essential singularities and the broken curve branch point singularities.

We note that this of the same form as (9) with $(y\psi_C)$ replacing y; hence the y series terminates in an essential singularity at a point given by

$$y_c\psi_C(y_c, z) = 1. \tag{29}$$

We can use the expansion (25) to deduce that at sufficiently low temperatures the curve of singularities is given by

$$y_c \simeq (1-z^2)^{-q/2}. \tag{30}$$

But it seems to us that the factor (30) will provide a dominant contribution to ψ_C over the whole range, and that ψ_C will behave in the same manner as ψ_R lowering the original curve of figure 8 so that it now bends away from the axis. Hence we will obtain a curve of essential singularities of the form indicated in figure 9 which intersects the branch point curve for ramified configurations at T_0.

It is very desirable to check the above conjecture by detailed numerical calculations. Two alternative approaches are being pursued; exact calculations of $\psi_{n,l}^{(i)}$ for small compact clusters of a given shape from which an asymptotic assessment may be possible (Binder and Guttmann, unpublished); and an extension of the series expansion (25) by the method outlined in the appendix.

The two curves shown in figure 9 represent the extreme limits of compactness and ramification. It seems reasonable to assume that other intermediate types of configuration will give rise to singularity curves lying between these limits.

We must emphasize again that in the above treatment, as in the Fisher treatment, the singularities refer only to the metastable phase. In equilibrium where no configurations are suppressed, singularities corresponding to a first-order transition would occur on the phase boundary.

8. Conclusions

Our first conclusion supports the Gibbs view that when $T>0$ there is an analytic extension beyond the phase boundary giving rise to a metastable phase. We have mentioned that Fisher's treatment, which ignores volume exclusion, should provide a reasonable approximation at sufficiently low temperatures. Our picture is consistent with this result since the analytic extension is short when T is small. However, Fisher's conclusion, that the singularity in the activity series coincides with the phase boundary, is rigorously correct only when $T=0$. We have defined a new temperature T_0 which can be understood physically as arising from the competition between compact and ramified clusters. The former are energetically favoured but have little entropy and therefore dominate at sufficiently low temperatures. The latter do not make economic use of energy but have large entropy, and are therefore favoured at higher temperatures. T_0 can be loosely described as the temperature of crossover from the dominance of compact clusters to that of ramified clusters.

When $T<T_0$ the phase terminates in an essential singularity. As Fisher (1967) has pointed out, a singularity of this kind would be extremely difficult to identify experimentally. By preventing clusters from growing beyond a specific size it should be possible to extend the phase beyond the singularity, and in this region the standard ideas of nucleation theory can be applied (Domb 1973).

When $T>T_0$ however, the phase terminates in a spinodal which is a singularity similar to a critical point, and should be clearly accessible to experimental observation.

There is good experimental evidence for the existence of spinodals (eg Chu *et al* 1969). In Fisher's picture they are non-thermodynamic (and are therefore described as 'pseudo-spinodals') whereas in our picture they represent the termination of the metastable thermodynamic phase. In a numerical analysis of low-temperature series for the Ising model, Gaunt and Baker (1970) were able to locate a spinodal curve near T_c and estimate its critical behaviour. Their evidence is clearly consistent with our analysis. However, a Monte-Carlo investigation (Binder and Müller-Krumbhaar 1974) failed to reveal a spinodal at the point predicted by Baker and Gaunt. The situation is therefore somewhat confused, and further investigations using series and Monte-Carlo methods would be welcome.

When excluded volume effects are significant we have found it convenient to focus attention on lattice configurations rather than on droplets or clusters, and we find that critical behaviour is determined by ramified configurations, since compact configurations are dampened out. This fits in with the analysis of Domb and Guttmann (1970) who found that the complexities of behaviour of low-temperature series for different lattices, which give rise to individual patterns of non-physical singularities, could reasonably be explained by taking account of Cayley tree configurations alone. It also enables one to understand why critical exponents are symmetric above and below T_c, since the high-temperature exponents are determined by series which are dominated by ramified configurations of various types (Domb 1972). Scaling theory then indicates that one should pass to low temperatures with the same configurations re-organized in a different manner.

Since a key characteristic of Curie point behaviour is long-range correlation, the suggestion that only ramified configurations play a part in its neighbourhood makes reasonable sense physically. These configurations extend over a much larger area than compact configurations, and if one wishes to 'communicate' over a long range it is inefficient to use compact configurations.

However, in the neighbourhood of T_c our treatment is not sufficiently refined to provide a detailed description of critical exponents and critical behaviour. In particular, no significance should be attached to the portion of the curve of singularities in figure 9 which extends to temperatures above T_c. The behaviour of the curve of singularities at T_c needs more careful attention.

We feel it important to distinguish between Curie point critical behaviour and percolation critical behaviour. The latter arise even in random mixtures with no energy of interaction, and will therefore be present in the Ising model even at infinite temperatures. The clusters which give rise to percolation are geometrical clusters, whilst those which give rise to Curie point behaviour are physical clusters in which the surface tension plays a major role. Therefore, whilst the statistical distribution of cluster size is immediately relevant to percolation critical exponents, we do not think that it has any direct connection with Curie point critical exponents.

The occurrence of percolation in Ising systems has been the subject of recent study (Müller-Krumbhaar 1974, Coniglio 1975) and it has been suggested that in three dimensions, since infinite clusters can occur at temperatures well below T_c, these might exercise an important influence on the physical behaviour of the Ising model. We do not feel this to be the case, since the occurrence of infinite clusters below T_c is a lattice-dependent property and does not arise, for example, in the hydrogen peroxide lattice with coordination number 3. According to current ideas of universality the behaviour of the ferromagnetic Ising model should not depend in any fundamental way on lattice structure.

We must finally discuss the general theorem of Lanford and Ruelle (1969) which applies to all systems with short-range forces. These authors showed that if the *stable* thermodynamic state is not analytic at a given point (as is the case in a first-order phase transition) then the assumption of analyticity in the multiple correlation functions leads to negative probabilities in at least one of them. If the latter possibility is excluded on physical grounds, then at least one of the multiple correlation functions must have a singularity. This theorem has been interpreted as excluding the possibility of metastable states in the strict thermodynamic sense for systems with short-range forces. However, the theorem does not necessarily conflict with the conclusions we have drawn above. The relationship between the theorem and our own work might be clarified if our configurational treatment were extended to the study of correlation functions. It would also help if more light were shed on the nature of the state to which the theorem applies, and whether the definition of metastability used in § 3 precludes its application.

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Appendix. Cluster integral calculation of interaction functions

For a lattice gas the function f_{ij}, which occurs in the Mayer cluster integrals, reduces to a series of δ-functions. A cluster integral then reduces to a cluster sum,

$$\frac{1}{n!}\sum f_{ij}f_{jk}\ldots f_{kl}, \tag{31}$$

over the vertices $i, j, k \ldots l$ of a connected graph. The function f_{ij} has the following values,

$$f_{ij} = -1 \tag{32}$$

when i and j are situated on the same lattice point;

$$f_{ij} = f = z^{-2} - 1 \tag{33}$$

when i and j are nearest neighbours on the lattice; f_{ij} is zero elsewhere. In case (32) we shall describe the interaction as a *pin*, and in the latter case as a *link*, following Temperley (1959).

For a graph with l edges the sum (31) consists of 2^l different terms corresponding to all possible combinations of pins and links, and each term can be related to one embedding in the lattice. (The method can be applied when all the interactions corresponding to different lattice bonds are different; in many respects it is convenient to deal with this general case, and subsequently make all the interactions equal.) We now sum the terms of all the different cluster sums which are related to one particular embedding; those which give rise to a function $\phi^{(i)}_{n,l}(y, z)$ for the embedding which can be calculated from finite cluster partition functions as illustrated in (15), (16), (17) and (21)

for the simplest embeddings ($\phi^{(i)}_{n,l}(y, z) = y^n z^s \psi^{(i)}_{n,l}(y, z)$). When we sum over all embeddings we obtain an expansion analogous to (14) but involving weak lattice constants $g_i(n, l)$ (cf (2)),

$$\ln Z = \sum_{l,n} g_i(n, l)\phi^{(i)}_{n,l}(y, z). \tag{34}$$

Let us focus attention on one particular embedding whose vertices are lattice points which we denote by Greek letters $\alpha, \beta \ldots \gamma$. We can expand $\phi^{(i)}_{n,l}$ as a power series in λ whose coefficients are polynomials in f. The lowest term is of order λ^n, and arises when $i, j \ldots k$ coincide in some re-arrangement with $\alpha, \beta \ldots \gamma$, and all the interactions are links. The $1/n!$ factor in (31) then disappears because of the $n!$ possible re-arrangements of $i, j \ldots k$, and this term can then be evaluated as $\lambda^n f^l$.

For a term in λ^{n+1} two of the vertices $i, j \ldots k$ must coincide with one of $(\alpha, \beta \ldots \gamma)$. Starting with our original λ^n configuration, we must enumerate all possible ways of introducing one additional vertex. There are two alternative possibilities, (*a*) select one of $(\alpha, \beta \ldots \gamma)$, introduce a new vertex coincident with it and connect the new vertex to $(\alpha, \beta \ldots \gamma)$ by pins or links, (*b*) decompose one of the old vertices into two parts, and connect other vertices by pins or links. The different interaction graphs arising from these alternatives are illustrated diagrammatically in figure 10 for a compact embedding, where links are denoted by solid and pins by dashed lines. The permutation factor cancels again, and for compact lattice constants all graphs of type (*b*) group together in pairs with equal and opposite signs; we therefore obtain a total contribution $-n\lambda^{n+1}f^l$.

For a term in λ^{n+2} two new vertices must be introduced and connected in all possible ways among themselves and to $(\alpha, \beta \ldots \gamma)$ by pins or links. The problem becomes more complicated and we shall not list all the possible new diagrams. It is easy to see that their total number is of order n^2, and that the total number for r new vertices is of order n^r.

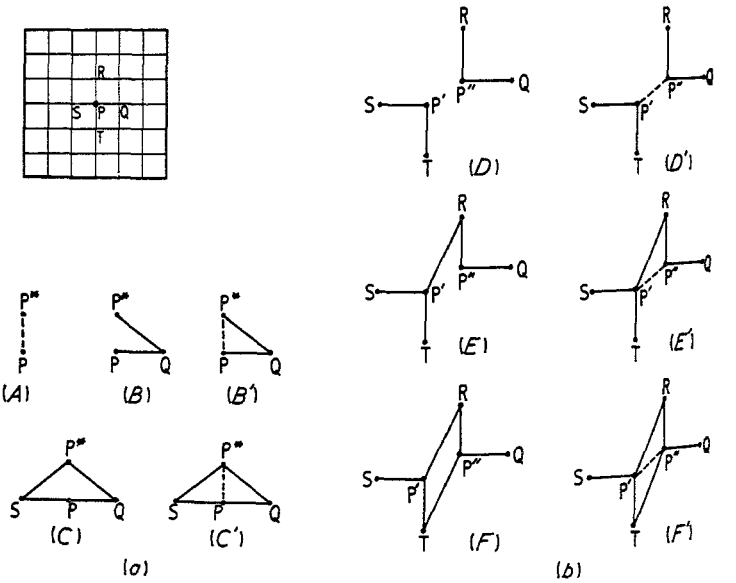

Figure 10. Examples of interaction diagrams arising from the insertion of an extra vertex. (*a*) addition of a vertex P* at P; (*b*) decomposition of vertex P into P' and P''. Full lines represent links and broken lines represent pins. The pairs *B*, *B'*; *C*, *C'*; *D*, *D'*; *E*, *E'* and *F*, *F'* have opposite signs and cancel.

From this we conclude that equation (22) is valid for a compact cluster, with $\psi_c(y, z)$ given by (25).

It is useful as an illustration of the method outlined above to reproduce the expansions for simple clusters given in (16), (17) and (21).

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