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Percolation, Droplet Models, and Spinodal Points

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A modified droplet model is proposed that incorporates both compact fluctuations that give rise to weak singularities at the first-order transition, and ramified fluctuations that give rise to spinodals in high dimensions. Renormalization-group considerations and studies of the percolation problem allow the use of ramified fluctuations to calculate spinodal exponents for $d>8$. The problem in lower dimensions is also discussed together with possible interpretation of these exponents in light of the indeterminacy in locating spinodal points.

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Mean-field theories (MFT) of the first-order phase transition[1] and the metastable state (e.g., van der Waals) have two common characteristics:

(1) The metastable state is describable by analytic continuation of stable-state thermodynamic functions *through* the first-order transition point; in other words, there are no precursors to first-order phase transitions in MFT.

(2) The metastable region (where the system is in a local free-energy minimum) and the spinodal region (where the system is unstable) are in MFT separated by a sharp line on which the thermodynamic functions are singular. These singularities are in some ways similar to those that occur at the critical point. In particular, the isothermal susceptibility diverges as one approaches the spinodal line in MFT.

The expectation that these two mean-field characteristics are also exhibited in more realistic systems has increasingly come into question. Droplet-model approximations,[2-4] renormalization-group (RG) calculations,[5,6] and series analysis[7,8] have all indicated that there is a very weak singularity as the coexistence curve is approached which prohibits analytic continuation through the first-order transition line (i.e., there is a very weak precursor to the first-order transition).

More recently, the existence of the spinodal in few dimensions has been questioned. Although RG calculations have indicated the possible presence of MFT spinodals[9,10] for $d>6$, the numerical and experimental evidence for MFT-like spinodals[11] in $d=2$ and 3 is ambiguous. It is in fact not at all clear that the notion of a spinodal point has a well-defined meaning, a point we will return to later.

The classical-droplet-model (CDM) approximation[2] appears to give an accurate description of the singularity at the first-order transition[7,8]; however, it shows no trace of spinodal singularities. This appears to be also true in several dimensions ($d>6$) where MFT appears to be describing the physics of spinodals properly[9,10] and one might expect thermodynamic singularities. In fact there is at present no theory of the first-order transition and the associated metastable state that is capable of describing both the precursor effects and the spinodal line.

In this Letter I propose a first step toward such a theory in the form of a new droplet model. Although the approach is not rigorous, I believe that it correctly describes the physics of spinodal singularities and is a meaningful first step toward a more complete theory.

In order to explain the modified droplet model (MDM) I will briefly describe the CDM approximation for an Ising model with a Hamiltonian

$$-\beta H = H\sum_i S_i + K\sum_{\langle ij\rangle} S_i S_j, \tag{1}$$

where $\beta = 1/k_B T$ and the sum $\sum_{\langle ij\rangle}$ is over nearest-neighbor pairs. For $T \ll T_c$, the critical temperature, we expect a magnetization per spin $m \sim 1$ with very improbable fluctuations of overturned spins. For $T \ll T_c$ the shape of the dominant fluctuations of overturned spins is determined by energy minimization[12] considerations which indicate that they form compact domains. (Compact domains are defined as clusters of S spins that have a surface proportional to $S^{(d-1)/d}$ in d dimensions.) Since the fluctuations are so rare, they can be considered to be noninteracting.

It is now straightforward to show[13] that the CDM free energy is

$$f(H,K) = \sum_{S=1} \exp[-HS - KS^{(d-1)/d}]. \tag{2}$$

The structure of Eq. (2) has been discussed extensively elsewhere.[2,6] I only mention that the free energy in Eq. (2) has an infinitely differentiable singularity and branch point at $H=0$.

The singularity in the CDM agrees with that found in analysis of series expansions for Ising models[7,8]; however, no trace of a spinodal occurs in the CDM in any dimension. The source of the difficulty is that noncompact fluctuations are incorrectly neglected for $H \neq 0$.

For any $H \neq 0$, no matter how small, the droplet size S will become large enough so that $HS \gg KS^{(d-1)/d}$. In this regime the exponential damping in Eq. (2) is dominated by the volume term and surface shapes become less important.[14] Moreover, the entropy available when such large fluctuations assume noncompact shapes becomes considerable. It is probable therefore that for $H \neq 0$ and S large enough, ramified rather than compact fluctuations dominate. [Ramified fluctuations of size S are those whose surface is proportional to S^σ where $(d-1)/d < \sigma < 1$. If $\sigma = 1$, the fluctuations are fully ramified.] The suggestion that ramified fluctuations are connected with spinodals was first made by Domb.[15] My approach differs from Domb's in several essential points discussed below.

Support for this point of view is found in RG flows. Consider, for example, the RG flow for the nearest-neighbor Ising model schematically represented in Fig. 1 where I have used the Migdal-Kadanoff[16,17] bond-moving transformation.

For $K > K_c$, $H \simeq 0$, the first few renormalizations increase both K and H until a critical value of the ratio of the renormalized coupling constants $K^{(n_0)}/H^{(n_0)} \sim 1$ is obtained after n_0 iterations.[6] Further iterations decrease K until the stable fixed point $K=0, H=\infty$ is reached.

The essential point is that renormalized free energies contain only those fluctuations present in the unrenormalized free energy on a length scale greater than b^n where b is the rescaling length and n the number of iterations of the RG. The fact that for n very large we have a renormalized coupling constant $K' \simeq 0$ implies that the fluctuations at this length scale (b^n) in the unrenormalized free energy are highly entropic.

The change from increasing to decreasing K under renormalization occurs at $K^{(n_0)}/H^{(n_0)} \simeq 1$ which implies that $b^{(n_0)}$ is the mean size of the largest compact droplets, or the critical size is $S_c = b^{n_0 d}$. From the RG transformations[5,6] $K' = b^{d-1}K$ and $H' = b^d H$ valid for $K^{(n_0)}/H^{(n_0)} = 1$ we obtain $S_c \sim (K/H)^d$. To summarize: The RG flows indicate that below a critical length scale $l_c = S_c^{1/d} \simeq K/H$ the dominant fluctuations are compact and above this length scale the ramified fluctuations dominate. The picture differs from Domb's in which ramified clusters dominate on all length scales for $T \neq 0$. This difference is reflected in the presence of a weak singularity as $H \to 0$ in the MDM and its absence in Domb's picture.

These considerations lead to the following modified form of the droplet-model free energy:

$$F(H,K) = \sum_{s=1} C(K/H,S) \times \exp[-HS - KS^{(d-1)/d}] + \ln\Xi. \tag{3}$$

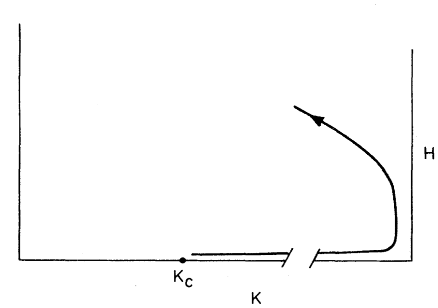

FIG. 1. Schematic RG flow in Migdal-Kadanoff approximation for nearest-neighbor Ising model.

In Eq. (3) $C(K/H,S)$ is a cutoff function that allows $\ln\Xi$, the part of the free energy that includes the effect of the ramified fluctuations, to dominate for $S>(K/H)^d$. The first term in Eq. (3) has been discussed elsewhere[6,18] as has the effect of various choices for $C(K/H,S)$.[19] I only mention here that the first term in Eq. (3) has singular behavior only slightly different from that of the CDM as $H\to 0$.[6,18] In the remainder of this Letter I will concentrate on the second term in Eq. (3). I note the following points: (1) I will take the ramified droplets to be noninteracting except for a possible excluded-volume contribution. This is indicated by the RG flow to an infinite-temperature fixed point for $H\neq 0$ (Fig. 1). (2) The choice of which class of fluctuations to include in the second term of Eq. (3) which I call the *ramified* free energy is also dictated by the RG flows. The statistics of clusters of overturned spins connected by nearest-neighbor bonds in the neighborhood of $H=\infty$, $T=\infty$ are known. In percolation this is referred to as the lattice animal problem.[20,21a] It is the lattice animals that form the droplets for our ramified free energy.

We know[20] that lattice animals are fully ramified so that the surface is proportional to the volume (i.e., $\sigma=1$). The number of lattice animals with S sites is also known; however, these statistics are only applicable when the animals are independent. We must consider therefore a possible excluded-volume effect. The arguments I employ are quite familiar in polymer physics.[21] Here I follow de Gennes.[21b]

Consider two clusters, A and B. The repulsive interaction between any two sites in different clusters can be written as $u(ij)=v\delta(R_{ij})$ where v is a strength parameter. The mean interaction per spin of two clusters occupying the same region of space is therefore given by

$$\sum_{j\in B}\langle u(ij)\rangle = v\sum_{j\in B}\langle\delta(R_{ij})\rangle \sim vS^2/S^{d/d_f},$$

where $S^2/S^{d/d_f}$ is the mean number of sites in cluster B that interact with site i in cluster A and d_f, the fractal dimension,[20] is defined by $l^{d_f}=S$ where l is the cluster diameter. For[20] $d>8$, $d_f=4$ and $d/d_f>2$ so that the cluster interaction is zero in the limit $S\to\infty$. For $d=2$ and 3, $d_f=\frac{3}{2}$ and 2, respectively,[22] so that the interaction energy is infinite.[23] For $d=4-7$, the Flory formula[24] $d_f=2(d+2)/5$ gives a good[21a] approximation for d_f. The Flory result gives $d/d_f<2$ in this range. For[23,24] $d=8$, $d/d_f=2$.

For $d>8$ therefore we can use lattice-animal statistics. The number of clusters of size S is then given by

$$n_S\sim e^{wS}/S^{5/2}, \tag{4}$$

where w is a known function[25] of d. It is now simple to show[14] that the singular part of the free energy generated by the fully ramified droplets is given by

$$F_R=\ln\Xi=\sum_{S=1}\exp[-(H+K-w)S]/S^{5/2}. \tag{5}$$

As mentioned above, the classical, and our modified, droplet models are low-T (high-K) approximations.[2,13] The parameter w is fixed by geometry and lattice type and is finite[25] (for example, w is monotonically increasing and for $d=9$, $w\approx 4$). Consequently in the range of validity of these droplet models we certainly have $K>w$. I am interested in the singular behavior of F_R which can occur only for H negative. As H approaches $H_c=-(K-w)$ from above along the real H axis the sum in Eq. (5) can be converted to an integral via the substitution $t=(H+K-w)S$. The conversion will not affect the singular behavior of F_R.[26] The divergence in the isothermal susceptibility as $H\to H_c$ is obtained from

$$\chi_T=(H-H_c)^{-1/2}\int_0^\infty(e^{-t}/t^{1/2})\,dt, \tag{6}$$

so that $\chi_T\sim(H-H_c)^{-1/2}$ or $\gamma_S=\frac{1}{2}$. Similarly we obtain $\beta_S=\frac{1}{2}$ and $2-\alpha_S=\frac{3}{2}$, which characterize the singular behavior of the magnetization and free energy as $H\to H_c$. These exponents are also those that are obtained in a mean-field theory.[9] Treatment of the problem for $d<8$ must include the excluded-volume effect. This is being pursued.

These considerations of singularities must be discussed in light of the indeterminacy inherent in the notion of spinodal points.[27] One way of examining the problem is to construct a restricted partition function in the spirit of Penrose and Lebowitz.[1] In this method all configurations are eliminated from the sum that contain fluctuations that nucleate the system into the stable phase. From Eq. (3) and physical considerations the fully ramified droplets I consider cannot nucleate the stable phase and therefore can be unambiguously kept in any restricted sum. Compact fluctuations, however, are a more complicated case. One can certainly keep compact droplets up to some critical size; however, one could also keep compact droplets up to any arbitrary *finite* size.

This arbitrariness reflects the "fuzziness" of the characterization and measurement of the metastable state as one moves away from the coexistence curve.

As discussed above, however, the spinodal exponents for $d > 8$ involve only fluctuations which are fully ramified and which can be unambiguously kept in any restricted partition function. This implies that the spinodal *exponents* are not dependent on what restrictions are used. The same, however, cannot be said about the spinodal temperature and amplitudes. In analogy with critical phenomena these quantities also depend on the physical characteristics of the system at short length scales (i.e., of the diameter of nucleating droplets near the spinodal) and hence will depend on the particular restriction used. I conclude that if the spinodal can be reached experimentally,[11] the spinodal temperature and amplitude of divergences will depend on how the experiment is done but the exponents will be universal.

In conclusion I have introduced a new droplet model that incorporates both fully ramified and compact fluctuations. This model exhibits a weak singularity at the coexistence curve as well as classical spinodals for $d > 8$ where MFT seems to be correct. These spinodals are characterized by universal exponents that are obtained by the association of the problem via RG with a percolation problem; however, the location of the spinodal point and amplitudes of singularities are not independent of the theory (i.e., restrictions) or the method of performing the experiment. In few dimensions the ramified fluctuations have an important excluded-volume effect that may strongly modify the behavior found in several dimensions. It is also interesting to note that this work combined with the work of Parisi and Sourlas[23] indicates a possible connection between spinodals and the Lee-Yang edge singularity.[28]

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[1]O. Penrose and J. L. Lebowitz, J. Stat. Phys. 3, 211 (1971).

[2]J. S. Langer, Ann. Phys. (N.Y.) 41, 108 (1967).

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

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

[5]W. Klein, D. J. Wallace, and R. K. P. Zia, Phys. Rev. Lett. 37, 639 (1976).

[6]W. Klein, Phys. Rev. B 21, 5245 (1980).

[7]G. A. Baker and D. Kim, J. Phys. A 13, L103 (1980).

[8]I. G. Enting and R. Baxter, J. Phys. A 13, 3723 (1980).

[9]J. D. Gunton and M. C. Yalabik, Phys. Rev. B 18, 6199 (1978).

[10]G. Dee, J. D. Gunton, and K. Kawasaki, J. Stat. Phys. 24, 87 (1981).

[11]K. Binder, Ann. Phys. (N.Y.) 98, 390 (1976).

[12]L. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, London, 1958).

[13]F. H. Stillinger, J. Chem. Phys. 38, 1486 (1963).

[14]W. Klein, to be published.

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

[16]A. A. Migdal, Zh. Eksp. Teor. Fiz. 42, 1457 (1975) [Sov. Phys. JETP 42, 743 (1975)].

[17]L. P. Kadanoff, Ann. Phys. (N.Y.) 100, 359 (1976).

[18]W. Klein, unpublished.

[19]R. K. P. Zia, Z. Phys. B 41, 129 (1981).

[20]D. Stauffer, Phys. Rep. 54, 1 (1979).

[21a]T. Lubensky and J. Isaacson, J. Phys. (Paris), Lett. 41, L469 (1980).

[21b]P. G. de Gennes, Nuovo Cimento 7, 363 (1977).

[22]F. Family, J. Phys. A 13, L325 (1980).

[23]G. Parisi and W. Sourlas, Phys. Rev. Lett. 46, 871 (1981).

[24]P. Flory, *Principles of Polymer Chemistry* (Cornell Univ. Press, Ithaca, 1971), Chap. XII.

[25]D. S. Gaunt, J. Phys. A 13, L97 (1980).

[26]L. Schulman, private communication.

[27]These considerations arose and were clarified in extensive conversations with K. Binder.

[28]M. E. Fisher, Phys. Rev. Lett. 40, 1610 (1978).