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On the Nature of the Nearest Singularities of the Free Energy in the Neighborhood of a Critical Point

Michael Coopersmith[1]

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Algebraic functions are used to provide an example of multiple-valued functions which coincide with a model (single-valued) free energy on one sheet of the Riemann surface in the neighborhood of a critical point. For the case of homogeneous free energies and $\alpha = \alpha' = 0$, there are enough conditions to determine the behavior of the nearest singularities (branch points) to the critical point of the algebraic function. If no other singularities are present these branch points would represent the spinodal line. The particular exponents of the two-dimensional Ising model are used to provide a specific example.

KEY WORDS: Algebraic function; branch points; critical point; free energy; Ising model; Riemann surface; singularity; spinodal line.

1. INTRODUCTION

The purpose of this paper is to present an example of the use of algebraic functions as models for the free energy in the neighborhood of a critical point. The example chosen has the critical exponents of the two-dimensional Ising model. It will be shown that the nearest branch points to the critical point have square root behavior, a result which holds in general for homogeneous algebraic functions which correspond to the critical exponents α and α' having the value zero.

Since the method we will use was presented a number of years ago we will begin with a review of the mathematical description.(1,2) This will be done in the next section. In Section 3 we will use the critical exponents of the two-dimensional Ising model(3) to construct a specific example of an

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[1] Department of Physics, University of Virginia, Charlottesville, Virginia 22901.

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algebraic function. In Section 4 we elaborate on the analytic behavior in order to demonstrate that the free energy does not violate certain analyticity conditions given by Lee and Yang.$^{(4)}$ Finally, in Section 5 we discuss the implications of the result for systems with other critical exponents and possible generalizations.

2. MATHEMATICAL PRELIMINARIES

Our starting point is a mathematical description of the free energy of a system in the neighborhood of a critical point. We choose that thermodynamic potential whose natural variables are naturally intensive. For example, for a liquid–vapor system we can look at the Gibbs free energy per particle (G/N = chemical potential μ) as a function of pressure and temperature. For a ferromagnet we look at that free energy which is a natural function of applied magnetic field H and temperature T. In either case the qualitative mathematical feature is that the isotherms of the free energy (which we shall refer to as F) have a continuous derivative for $T > T_c$ and a discontinuous derivative at a particular value of the field variable (pressure in the case of a fluid) for $T < T_c$.

We will now take as our definition of a critical point the following generalization of van der Waals thesis title (On the Continuity of Liquid and Vapor States).$^{(5)}$ Our generalization is given by the insertion of the word "analytic" before "continuity" so that we have the phrase "analytic continuity of liquid and vapor states." By this we mean that the free energy is an analytic function on the real H and T axes with a singularity at the critical point ($H = 0$, $T = T_c$) and a possible line of singularities on the coexistence curve ($H = 0$, $T < T_c$) such that F has a discontinuous derivative in H. Thus we have

$$M_+ = -\left.\frac{\partial F}{\partial H}\right|_{H\to 0+} \neq -\left.\frac{\partial F}{\partial H}\right|_{H\to 0-} = M_-$$

Despite the apparent complication of the foregoing description, there is actually a well-known class of functions which can exhibit the desired behavior. These functions are known as algebraic functions and are multiple valued with branch points (fractional power, positive or negative) as their only singularities.$^{(6)}$ The way they effect a discontinuous derivative is illustrated by the Weiss molecular field theory$^{(7)}$ or equivalently van der Waals equation of state. Van der Waals equation of state is actually a third-order algebraic equation defining the density implicitly. However, the Weiss molecular field theory defines the corresponding quantity (magnetization) as a solution to a transcendental equation. This brings us to the main point of the discussion. Obviously we cannot claim that any free energy is an algebraic function even if the critical exponents are rational.

Clearly, the Weiss molecular field theory already violates such an assertion. However, algebraic functions are examples of a class of multiple-valued functions whose Riemann surface might be related to the Riemann surface of the free energy of actual models in the neighborhood of the critical point if such a Riemann surface exists, i.e., if the true free energy is analytically continuable onto more than one sheet. Evidence for and against such a continuation has been given, respectively, by the author(8) and by R. B. Griffiths.(9) In addition, previous work by Fisher and Langer on the one-dimensional droplet model has shown that there can be an essential singularity in the density at the condensation point below T_c.(10,11) However, these essential singularities are continued above T_c and thus the free energy, although single valued, does not satisfy the hypotheses of Ref. 8. Although such a free energy remains a distinct possibility, we feel that a result of this nature violates the physical spirit of a critical point which is the indistinguishability of the liquid and vapor phases above T_c. The absolute distinguishability was noted by Fisher in Ref. 10.

The singularities (branch points) of the algebraic function in the neighborhood of the critical point approach the critical point as the temperature approaches the critical temperature. It is well known that the Weiss molecular field theory free energy has square root branch points which approach the critical point. These lead to a finite magnetization at zero applied field when $T < T_c$. It is also well known that there are solutions to the transcendental equation which yield a finite magnetization at zero applied field for all temperatures. These solutions, however, represent branches which are not connected to the three branches which give the physical values in some finite neighborhood of the critical point. Thus we can speak of the appropriate third-order algebraic function as equivalent to the Weiss molecular field theory in this neighborhood. This algebraic function is given by

$$P(F,H,t) = F\left(F + \tfrac{3}{4}t^2\right)^2 + \left(\tfrac{27}{8}Ft + \tfrac{9}{32}t^3\right)H^2 + \tfrac{81}{64}H^4 = 0 \qquad (1)$$

where $t = T - T_c$.

Three isotherms are shown in Fig. la and two isochamps are shown in Fig. 1b. It is easy to imagine a generalization of the third-order polynomial representing the molecular field theory to higher-order polynomials which would have the same general characteristics on the real t and H axes but with different order branch points and thus different critical exponents. The problem comes in determining whether the general characteristics place any restrictions on the types of algebraic functions one can have. The specific features of algebraic functions are notoriously hard to ascertain and until the present instance this description was devoid of any practical content except to provide a picture of possible branch point behavior. In

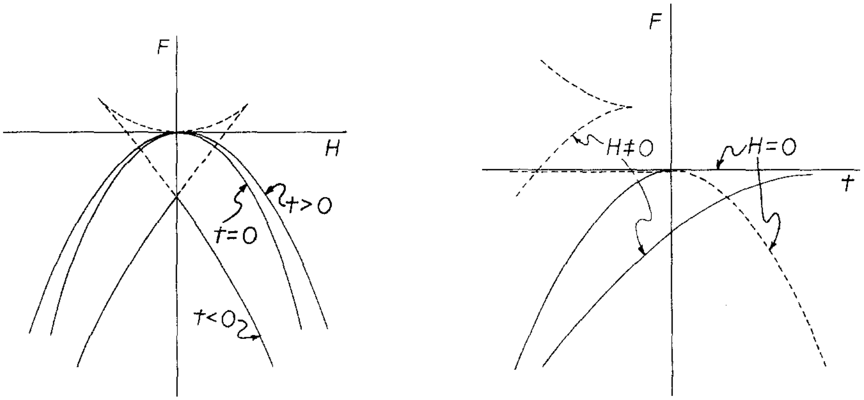

Fig. 1. Three isotherms of F vs. H and two isochamps of F vs. t for the molecular field theory. The dashed lines show nonphysical values.

the next section we shall show how the form of the algebraic function modeling the two-dimensional Ising model free energy is self-restricting to the point of providing information about the nearest nonphysical singularities (the so-called spinodal line). In the following discussion we will use the term "physical sheet" to denote the complex H plane for real t which contains the single-valued function defined as that part of the multiple-valued function which coincides with the physical (thermodynamically stable) free energy on the real H axis and has the analytic properties previously mentioned.

3. EXAMPLES OF ALGEBRAIC FUNCTIONS

The problem of determining the singularities (branch points) of an algebraic function boils down to finding the roots of the discriminant of the defining polynomial. Since the discriminant of even a very low-order polynomial can be of order greater than four, it follows that no closed solutions can be obtained unless the factorization is obvious. It would thus appear that a polynomial representing the two-dimensional Ising model (which, as we shall see, is of order 15) would be hopelessly intractable. That this is not the case is the subject of this paper.

We begin by illustrating the use of the discriminant for the third-order polynomial representing the molecular field theory. Suppose that we wish to find the form of a third-order polynomial representing the graphs of Fig. 1. If we specialize to a free energy which is homogeneous in t and H then $P(F,H,t)$ is also homogeneous in F, t, and H. If we also specify that

$\alpha = \alpha' = 0$, $\beta = 1/2$ and $\gamma = \gamma' = 1$, the critical exponents of the molecular field theory, then the polynomial must have the form

$$P = F(F + t^2)^2 + (at^3 + bFt)H^2 + H^4 = 0 \tag{2}$$

where a and b are numbers to be determined. The discriminant is a 4×4 determinant each element of which is related to one of the coefficients of F, which coefficient is itself a polynomial in t and H^2. However, we observe that, regarded as a function of H^2, the polynomial in Eq. (2) is quadratic with coefficients which are polynomials in F and t. Thus we have

$$P = G^2 + (at^3 + bFt)G + F(F + t^2)^2 = 0 \tag{3}$$

where $G = H^2$. The isotherms of G look like Fig. 2. The cusp (branch point) is still present but the crossing point has turned into parabolic form. The discriminant is now the familiar radical $b^2 - 4ac$ in the solution of the quadratic equation $ax^2 + bx + c = 0$. For the polynomial of Eq. (3) this is

$$D = (at^3 + bFt)^2 - 4F(F + t^2)^2 \tag{4}$$

Since there is only one cusp, this implies that there is only one (multiple) root of $D = 0$. Thus, we require that

$$\begin{aligned} D &= -4F^3 + (b^2 - 8)t^2F^2 + (2ab - 4)t^4F + a^2t^6 \\ &= -4(F - F_0)^3 \end{aligned} \tag{5}$$

where F_0 is the root giving the position of the cusp. Equation (5) determines

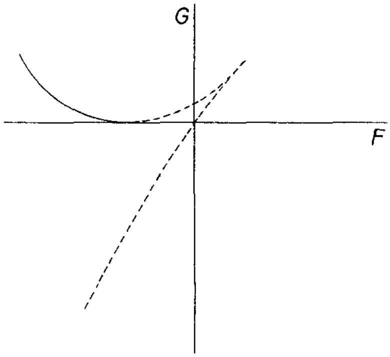

Fig. 2. An isotherm for $t < 0$ of G vs. F for the molecular field theory. The dashed lines show nonphysical values.

a, b, and F_0:

$$4F_0^3 = a^2 t^6 \tag{6a}$$

$$-12F_0^2 = (2ab - 4)t^4 \tag{6b}$$

$$12F_0 = (b^2 - 8)t^2 \tag{6c}$$

The solution is

$$a = \frac{2\sqrt{3}}{9} \tag{7a}$$

$$b = 2\sqrt{3} \tag{7b}$$

$$F_0 = \tfrac{1}{3}t^2 \tag{7c}$$

With the values of a and b given by Eq. (7), Eq. (2) is equivalent to Eq. (1) if we make the simple linear substitution $t \to (\sqrt{3}/2)t$ and $H \to (3\sqrt{2}/4)H$. The molecular field theory can thus be regarded as that homogeneous free energy whose Riemann surface is given by that of a third-order algebraic function with only two cusps (branch points). This completely determines the coefficients of the defining polynomial.

As an example of what might be considered "molecular field theories" in this mathematical scheme, consider the free energy whose isotherms are given by Fig. 3. Such a free energy would have no discontinuity in its specific heat. In this case the function F has three branches with the same

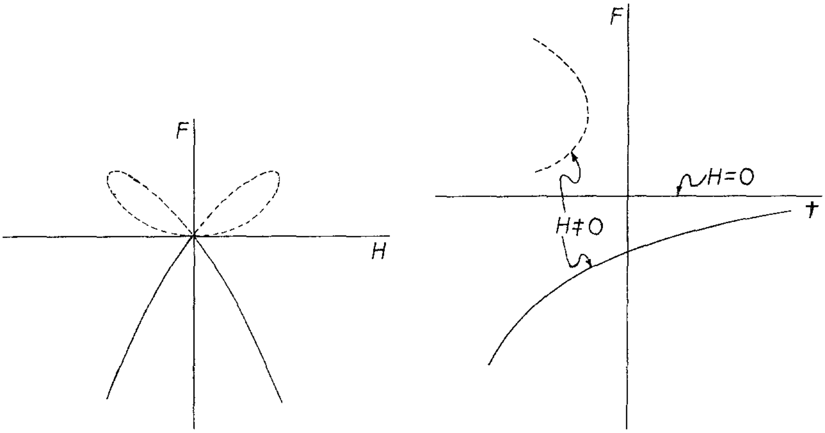

Fig. 3. An isotherm for $t < 0$ of F vs. H and two isochamps of F vs. t for a "molecular field theory" with no discontinuity in the specific heat. The dashed lines show nonphysical values.

value (zero) at $H = 0$ so that the homogeneous polynomial is given by

$$P = F^3 + (at^3 + bFt)H^2 + H^4 = 0 \tag{8}$$

Again, regarding the polynomial P as a quadratic function of H^2, we have

$$P = G^2 + (at^3 + bFt)G + F^3 = 0 \tag{9}$$

The discriminant is given by

$$\begin{aligned} D &= (at^3 + bFt)^2 - 4F^3 \\ &= -4F^3 + b^2t^2F^2 + 2abt^4F + a^2t^6 \end{aligned} \tag{10}$$

If we try to set D equal to $-4(F - F_0)^3$ as before to ensure one branch point, we find

$$4F_0^3 = a^2t^6 \tag{11a}$$

$$-12F_0^2 = 2abt^4 \tag{11b}$$

$$12F_0 = b^2t^2 \tag{11c}$$

It is easily seen that these equations are incompatible since Eq. (11b) squared yields $36F_0^4 = a^2b^2t^8$, whereas Eq. (11a) multiplied by Eq. (11c) gives $48F_0^4 = a^2b^2t^8$. Thus no nontrivial solution exists. The reason is obvious since the discriminant is of the form $(1 + x)^2 - ax^3$, which cannot be a perfect cube. We also see from Fig. 4 that there is a crossing point at $F = 0$ which must show up as a root of the discriminant. In order to get a root representing the branch point we must have $a = 0$. There is a physical (thermodynamic) reason for this which will be discussed later when we take

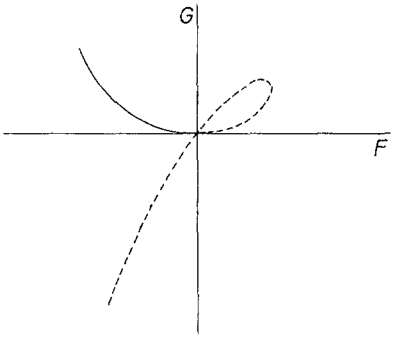

Fig. 4. An isotherm for $t < 0$ of G vs. F for the "molecular field theory" of Fig. 3. The dashed lines show nonphysical values.

up the general case. The discriminant is then

$$\begin{aligned} D &= -4F^3 + b^2t^2F^2 \\ &= F^2(b^2t^2 - 4F) \end{aligned} \tag{12}$$

and we can put $b = 1$. The algebraic function describing Fig. 3 is then given by

$$P = F^3 + H^2tF + H^4 = 0 \tag{13}$$

Note that the branch point in Fig. 3 is not in the same place as the branch point in Fig. 4 since it is not a cusp.

The generalization to non-molecular-field-theory values of the critical exponents (higher-order algebraic functions) is obvious at this point but the details are more intricate and require further elaboration. We will restrict the discussion in this paper to the case where $\alpha = \alpha' = 0$ and the free energy is a homogeneous function of H and t. The particular case of the two-dimensional Ising model will be used since the exponents are known and there is no discontinuity in the specific heat. Although the two-dimensional Ising model has a logarithmic singularity in the specific heat, this could be incorporated into our example without changing the basic structure of the Riemann surface. In mathematical terms, a logarithmic singularity arises out of an Abelian integral using the algebraic function, hence the Riemann surface (and of necessity, the branch points associated with it) remains unchanged. We make this point because, although no claim is made that our example represents the actual topology of the Ising model free energy, it might be objected that it is too artificial.

Some observations are needed in order to generalize the previous result to higher-order algebraic functions. For the two-dimensional Ising model, the critical exponents which will determine the defining polynomial are $\alpha = \alpha' = 0$, $\beta = 1/8$. If the free energy is homogeneous in H and t then $\gamma = 2 - \alpha - 2\beta = 7/4$ and $\delta = (2 - \alpha)/\beta - 1 = 15$. More generally, we can expand the free energy around the coexistence curve ($H = 0$) and the critical isotherm to get

$$F = \sum_{i=0}^{\infty} a_i(t)H^i \tag{14a}$$

or

$$F = \sum_{i=0}^{\infty} b_i(H)t^i \tag{14b}$$

where $a_i(t)$ and $b_i(H)$ are given by

$$a_i(t) = t^{\alpha_i} \tag{15a}$$

$$b_i(H) = H^{\beta_i} \tag{15b}$$

with α_i and β_i defining the critical exponents. In particular, $\alpha_0 = 2 - \alpha$, $\alpha_1 = \beta$, $\alpha_2 = -\gamma$, $\beta_0 = 1 + 1/\delta$. Relations 14a and 14b provide a constraint on the defining polynomial as follows. The most general form for the polynomial defining the Riemann surface of the two-dimensional Ising model free energy is

$$P(F,H,t) = P_1(F,t) + P_2(F,t)H^8 + H^{16} \tag{16}$$

where

$$\begin{aligned} P_1(F,t) = F^3\big(&d_0t^{24} + d_1Ft^{22} + d_2F^2t^{20} + d_3F^3t^{18} + d_4F^4t^{16} \\ &+ d_5F^5t^{14} + d_6F^6t^{12} + d_7F^7t^{10} + d_8F^8t^8 + d_9F^9t^6 \\ &+ d_{10}F^{10}t^4 + d_{11}F^{11}t^2 + d_{12}F^{12}\big) \end{aligned} \tag{17a}$$

$$\begin{aligned} P_2(F,t) = {}&c_0t^{15} + c_1Ft^{13} + c_2F^2t^{11} + c_3F^3t^9 + c_4F^4t^7 \\ &+ c_5F^5t^5 + c_6F^6t^3 + c_7F^7t \end{aligned} \tag{17b}$$

Some explanation is in order. First, P_1 is a 15th-order polynomial in F and H^{16} is the corresponding homogeneous term because $\delta = 15$. (Recall that for $t = 0$, $F = H^{1+1/\delta} = H^{16/15}$.) Second, the only other power of H to occur is H^8 since, for $\alpha = 0$, there are no homogeneous terms involving any other integral powers of H than H^{16} for H^8. (Recall that $t \sim F^{1/2} \sim H^{8/15}$. Hence for H^4, say, the polynomial would have to contain $F^{45/4}H^4 \sim t^{45/2}H^4$ which is not an integral power of F or t.) Third, F^3 must be the lowest power of F in P_1 because there must be at least three branches of F having the value $F = 0$ at $H = 0$ for all t. (This ensures that $\alpha = \alpha' = 0$, that is, no discontinuity in the specific heat.)

We now apply the expansions given by Eqs. (14a) and (14b) to obtain further restrictions on P_1 and P_2. For $t > 0$, F is an even function of H. Thus

$$F = a_2(t)H^2 + a_4(t)H^4 + \cdots \tag{18}$$

Likewise, for $t < 0$, F has two branches each of which has a finite derivative (non-zero order parameter) at $H = 0$. Therefore F has the form

$$F = a_1(t)H + a_2(t)H^2 + \cdots \tag{19}$$

The problem is to reconcile these expansions with the form of P given by Eqs. (16) and (17). Clearly P_1 cannot have F^3 as the lowest power of F since $a_1(t)$ would be zero in Eq. (19). This is so because there is no other generator of H^3 in P. Hence the lowest power of F in P_1 must be F^8. But then the branch given by Eq. (18) would require that the lowest power of F in P_2 be F^4. Finally, the branch given by Eq. (19) then requires the lowest power of F in P_1 to be F^{12} in order to generate H^{12}. This scheme is now consistent as all the proper powers of H can be generated from the expansions of the two branches. P thus has the form

$$\begin{aligned} P = {} & F^{12}\left(d_0t^6 + d_1Ft^4 + d_2F^2t^2 + d_3F^3\right) \\ & + F^4\left(c_0t^7 + c_1Ft^5 + c_2F^2t^3 + c_3F^3t\right)H^8 + H^{16} \end{aligned} \tag{20}$$

Having found the form of $P(F,H,t)$ it is now necessary to determine the coefficients c and d. To do this we make an ansatz prompted by the molecular field theory. We will assume that there is only one cusp in F as a function of $G(=H^8)$. There will then be only one cusp in G as a function of F. This is equivalent to saying that the discriminant D is of the form

$$\begin{aligned} D = {} & F^8\left(c_0t^7 + c_1Ft^5 + c_2F^2t^3 + c_3F^3t\right)^2 \\ & - 4F^{12}\left(d_0t^6 + d_1Ft^4 + d_2F^2t^2 + d_3F^3\right) \\ = {} & -4d_3F^8\left(F + bt^2\right)^7 \end{aligned} \tag{21}$$

Without loss of generality set $d_3 = 1$ and $b = 1$. The two sets of real solutions are

$$\begin{array}{ll} c_0 = 2 & c_0 = -2 \\ c_1 = -7 & c_1 = 7 \\ c_2 = -35/4 & c_2 = -35/4 \\ c_3 = 35/8 & c_3 = 35/8 \\ d_0 = -35/64 & d_0 = 35/64 \\ d_1 = 119/64 & d_1 = -119/64 \\ d_2 = -567/256 & d_2 = 567/256 \end{array} \tag{22}$$

The second set corresponds to choosing t positive for temperatures above the critical temperature while the first set inverts this (t is negative for $T > T_c$). The polynomial $P(F,H,t)$ is therefore given by

$$\begin{aligned} P(F,H,t) = {} & F^{15} - \frac{567}{256}t^2F^{14} + \frac{119}{64}t^4F^{13} - \frac{35}{64}t^6F^{12} + \frac{35}{8}tH^8F^7 \\ & - \frac{35}{4}t^3H^8F^6 + 7t^5H^8F^5 - 2t^7H^8F^4 + H^{16} \\ = {} & G^2 + \left(\frac{35}{8}tF^3 - \frac{35}{4}t^3F^2 + 7t^5F - 2t^7\right)F^4G \\ & + \left(F^3 - \frac{567}{256}t^2F^2 + \frac{119}{64}t^4F - \frac{35}{64}t^6\right)F^{12} \end{aligned} \tag{23}$$

We now investigate the behavior of the singularities (branch points) on the nonphysical sheet. These correspond to the spinodal line in the molecular field theory. The values of H are given by solving $P(F,H,t) = 0$ with

$F = t^2$:

$$P(t^2, H, t) = \frac{25}{256} t^{30} + \frac{5}{8} t^{15} G + G^2 = 0 \tag{24}$$

$$G_0 = H_0^8 = -\frac{5}{16} t^{15} \tag{25}$$

For $t < 0$, two of the roots in H_0 lie on the real axis. They are

$$H_0 = \pm\left(-\tfrac{5}{16} t^{15}\right)^{1/8} \tag{26}$$

This is the spinodal line. The behavior of F in the neighborhood of these branch points is easily found by expansion. Solving Eq. (23) in its quadratic form, we have

$$G_0 + \Delta G = \tfrac{1}{2}\left\{ -P_1(F_0 + \Delta F, t) \pm \left[P_1^2(F_0 + \Delta F, t) - 4P_2(F_0 + \Delta F, t)\right]^{1/2}\right\} \tag{27}$$

where $F_0 = t^2$. Since P_1 and P_2 are polynomials, we can expand in powers of ΔF:

$$\begin{aligned} G_0 + \Delta G = \frac{1}{2}&\left[-P_1^{(0)} - \frac{\partial P_1^{(0)}}{\partial F}\Delta F - \frac{1}{2}\frac{\partial^2 P_1^{(0)}}{\partial F^2}(\Delta F)^2 - \cdots \right] \\ &\pm \frac{1}{2}\left[D^{(0)} \frac{\partial D^{(0)}}{\partial F}\Delta F + \frac{1}{2}\frac{\partial^2 D^{(0)}}{\partial F^2}(\Delta F)^2 + \cdots \right]^{1/2} \end{aligned} \tag{28}$$

where the superscript zeros indicate that the polynomial is evaluated at F_0 and t. Thus

$$\begin{aligned} \Delta G = -\frac{1}{2}&\left\{ \frac{\partial P_1^{(0)}}{\partial F}\Delta F + \frac{1}{2}\frac{\partial^2 P_1^{(0)}}{\partial F^2}(\Delta F)^2 + \cdots \right. \\ &\left. \mp \left[\frac{\partial D^{(0)}}{\partial F}\Delta F + \frac{1}{2}\frac{\partial^2 D^{(0)}}{\partial F^2}(\Delta F)^2 + \cdots \right]^{1/2}\right\} \end{aligned} \tag{29}$$

In the molecular field theory, D has the form $(F - F_0)^3$ so that the lowest power of ΔF inside the square root is $(\Delta F)^3$. In the present example, D has the form $(F - F_0)^7$ so that the lowest power of ΔF inside the square root is $(\Delta F)^7$. This still represents a cusp but the isotherm of M vs. H no longer has the familiar "loop" of molecular field theory. The reason is that, unlike the molecular field theory, M has a cusp as a function of H. That is, $M - M_0 = \Delta M \sim \Delta H + (\Delta H)^2 + (\Delta H)^{5/2} + \cdots$ rather than $\Delta M \sim (\Delta H)^{1/2} + \Delta H + \cdots$.

Our picture of the Riemann surface would now be complete were it not for the following annoying feature. Recall that in the molecular field

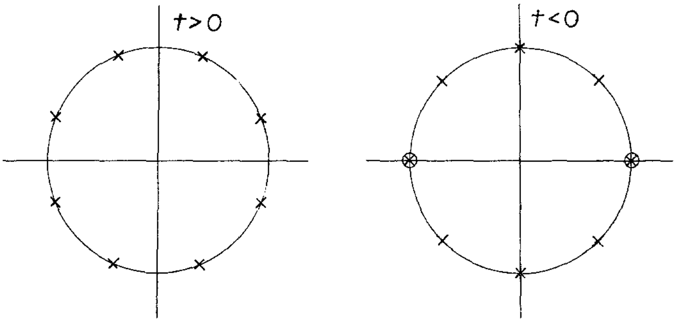

Fig. 5. Branch points in H vs. F for the free energy defined by Eq. (23). The circled branch points for $t < 0$ give the spinodal line.

theory the behavior of the nearest branch points is given by $H_0 \sim (-t)^{3/2}$. These branch points are thus on the real H axis for $t < 0$ and this constitutes the spinodal line while for $t > 0$ they are on the imaginary H axis. In the present example, $H_0 \sim (-t)^{15/8}$. The positions of these branch points for $t < 0$ and $t > 0$ are shown in Fig. 5. The two branch points on the real axis for $t < 0$ are not on the physical sheet and constitute the spinodal line, but for $t > 0$, two violations of the Yang–Lee theorem for the two-dimensional Ising model appear to occur. The first is that there are no singularities on the imaginary H axis and the second is that there appear to be singularities elsewhere on the physical sheet where they are forbidden to be. In the next section we shall show that both problems are resolved by further analysis of the function $F(H, t)$.

4. COMPLETE ANALYTIC BEHAVIOR OF THE LAST EXAMPLE

Although the previous analysis has the advantage of simplicity, it does not yield all the branch points of F as a function of H and t. The reason is

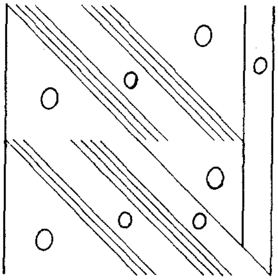

Fig. 6. Determinant giving the discriminant of the 15th-order polynomial of Eq. (23).

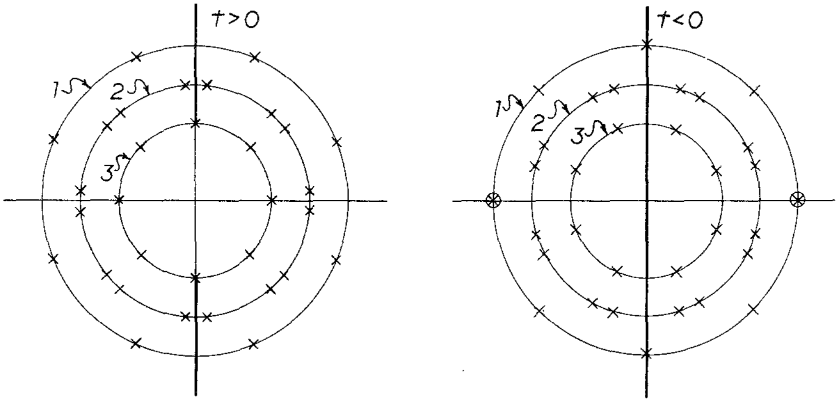

Fig. 7. Branch points of F vs. H for the free energy defined by Eq. (23) showing cuts in the H plane for $t > 0$ and $t < 0$. The circled branch points for $t < 0$ give the spinodal line.

that only cusps of H as a function of F will remain cusps of F as a function of H. Quadratic behavior (no branch point) of H as a function of F will become square root behavior (branch point) of F as a function of H.

To find all the branch points of $F(H, t)$ it is thus necessary to determine the roots of the discriminant of $P(F, H, t)$. Although the discriminant is the determinant of a 28 × 28 matrix it can be evaluated easily using MACSYMA, the computer program developed at MIT for manipulating algebraic expressions.[2] The matrix has the form shown in Fig. 6 and can be immediately reduced to a 25 × 25 matrix. The determinant is found to be a 22nd-order polynomial in $G(= H^8)$ whose lowest power is G^{12}. The roots are then given by

$$G = 0 \qquad (12 \text{ times}) \tag{30a}$$

$$G = -\frac{5}{16} t^{15} \qquad (7 \text{ times}) \tag{30b}$$

$$G = \frac{334{,}357}{33{,}554{,}432} t^{15} = 0.0099646 t^{15} \tag{30c}$$

$$G = (0.0548007 \pm 0.0212118 i) t^{15} \tag{30d}$$

The three roots given by Eqs. (30c) and (30d) represent branch points which were not previously found.

It remains to be demonstrated that the imaginary roots (branch points) given by Eq. (30c) for $t > 0$ lie on the physical sheet, while all the other branch points lie on other sheets. To do this, we used MACSYMA to make an

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[2] I am indebted to Dr. V. Emery of Brookhaven National Laboratory for calling my attention to MACSYMA.

"excursion" in the complex H plane starting at the origin and going radially outward toward the branch point. The branch points lie on three rings of radii $0.56|t^{15/8}|$, $0.702|t^{15/8}|$, and $0.86|t^{15/8}|$. Referring to Figs. 7a and 7b, which show all the branch points of F in the H plane for $t > 0$ and $t < 0$, we tabulate the results in Table I.

Our analysis is now complete. We conjecture that the analytic behavior of the nearest singularities to the critical point for the free energy of the two-dimensional Ising model is given by the Riemann surface of the

Table I

t	Ring	Angle	Value of F at branch point	Value of F on physical sheet	Branch point
>0	1	$\pm\frac{\pi}{8}$	real	complex	not on physical sheet
>0	1	$\pm\frac{3\pi}{8}$	real	complex	not on physical sheet
>0	2	0	$0.705 \pm 0.375i$	real	not on physical sheet
>0	2	$\pm\frac{\pi}{4}$	$0.705 \pm 0.375i$	$-0.097 \pm 0.351i$	not on physical sheet
>0	2	$\pm\frac{\pi}{2}$	$0.705 \pm 0.375i$	$0.578 \pm 0.367i$	not on physical sheet
>0	3	0	positive real	negative real	not on physical sheet
>0	3	$\pm\frac{\pi}{4}$	positive real	complex	not on physical sheet
>0	3	$\pm\frac{\pi}{2}$	positive real (0.49)	positive real (0.49)	on physical sheet (branch cuts from $\pm 0.56i$ to $\pm i\infty$)
<0	1	0	positive real	negative real	on analytic continuation of physical sheet (spinodal lines)
<0	1	$\pm\frac{\pi}{4}$	positive real	complex	not on physical sheet
<0	1	$\pm\frac{\pi}{2}$	positive real	complex	not on physical sheet
<0	2	$\pm\frac{\pi}{8}$	$0.705 \pm 0.375i$	$-0.766 \pm 0.320i$	not on physical sheet
<0	2	$\pm\frac{3\pi}{8}$	$0.705 \pm 0.375i$	$-0.310 \pm 0.877i$	not on physical sheet
<0	3	$\pm\frac{\pi}{8}$	real	complex	not on physical sheet
<0	3	$\pm\frac{3\pi}{8}$	real	complex	not on physical sheet

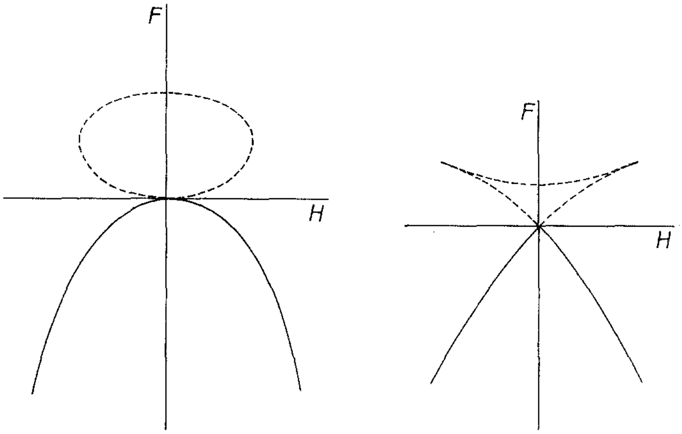

Fig. 8. Two isotherms for $t > 0$ and $t < 0$ of F vs. H for the free energy defined by Eq. (23).

algebraic function $F(H, t)$ determined by Eq. (23). Two isotherms for $t > 0$ and $t < 0$ are shown in Figs. 8a and 8b. What is truly extraordinary is that the free energy is molecular field like in the variable $G = H^8$.

5. DISCUSSION

The example we have just presented which has the critical exponents of the two-dimensional Ising model appears to be dependent on the detailed analysis of its singularity structure. Despite the apparent complication, it is easily seen that the feature responsible for the behavior of the nearest singularities is the fact that $\alpha = \alpha' = 0$. This is responsible for $P(F, H, t)$ being quadratic in H^8 in our present example and $P(F, H, t)$ being quadratic in H^2 for the molecular field theory. This in turn causes the nearest singularities to be square root branch points. The result, which we now state precisely does not depend on this ansatz.

Given an algebraic function of the form

$$P(F, H, t) = P_1(F, t) + P_2(F, t)H^{2n} + H^{4n} \qquad (n \text{ an integer})$$

which represents a free energy with $\alpha = \alpha' = 0$, then the nearest branch points to the origin ($t = H = 0$) have the form $(\Delta H)^{m/2}$ for fixed t, where m is an integer dependent on the precise form of P_1 and P_2.

To the extent that F does not have branch points which violate the Yang–Lee theorem and no other singularities are present, the nearest branch points would represent the spinodal line. In order to test this, for the two-dimensional Ising model for example, one would have to perform an analytic continuation of the physical free energy onto the nearest nonphysical sheet if such an analytic continuation exists. For a real system it is a matter of speculation at present whether the measured spinodal line (metastable state) coincides with the analytic continuation of the free energy and thus no prediction can legitimately be made for experimental measurement.

In future work we shall investigate the effect of imposing convexity as a condition on the function $F(H, t)$ to see if this further limits the behavior of the nearest singularities. Other investigations will include an attempt to relax the condition $\alpha = \alpha' = 0$ and removal of the scaling condition (nonhomogeneous free energies).

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