Michael H. Coopersmith

Department of Physics, Case Western Reserve University, Cleveland, Ohio (Received 21 March 1968; revised manuscript received 24 April 1968)

Using the idea that the thermodynamic potential, whose natural variables are intensive, is analytically continuable in all these variables from the liquid state to the vapor state, we have arrived at a picture of a phase transition which is in accord with all currently observed behavior in the neighborhood of a critical point. Using functions which are algebraic in both the applied field and the temperature, we have shown for a magnetic system that (a) Rushbrooke' s inequality holds with the equality sign as a consequence of the symmetry of the free energy in the applied field, and (b) there is a set of relations between the critical exponents of derivatives of the free energy higher than the second. Although they only lead to rational critical exponents, algebraic functions are uniquely suited to this problem since they automatically satisfy the requirements of analytic continuation. The homogeneous functions of Widom with rational critical exponents are shown to be a special case of these algebraic functions, and several examples are given which illustrate some apparently anomalous behavior, such as (a) the critical exponent β may have an odd denominator. (b) the critical exponent δ may have an even numerator, and (c) the primed and unprimed critical exponents may be unequal.

I. INTRODUCTION

Recently, Griffiths' has made use of thermodynamic potentials which are analytic in both arguments to describe the behavior of idealized ferromagnets and fluids in the neighborhood of the critical point. Such a proposal has some far reaching consequences which were only hinted at in Ref. 1, mainly because full use was not made of the consequences of analyticity in more than one variable. The purpose of this paper is twofold. First, to elaborate on the above assumption and demonstrate its intimate connection with the very existence of a phase transition with a critical temperature and what van der Waals' termed the "continuity of the liquid and vapor states". Second, to show some of the direct consequences of Griffiths' assumption with regard to the so-called scaling laws relating various critical exponents. We shall see that certain scaling laws are independent of the particular function used to represent the thermodynamic potential while others are not, so that, in a very real sense, those scaling laws which are invariant describe the "thermodynamics" of the situation, since the force laws do not enter into them. Our point of view, then, is unashamedly patterned after that given by Chew' with respect to field theory, that is, to regard the generating function for the observables as being analytic in whatever independent variables there are, and deduce all the consequences thereof. Analyticity is in this sense regarded as a separate physical law, the object being not to justify it, but to test its predictions. We might add that in thermodynamics, at least, a proof of the analyticity of the thermodynamic potential for a given Hamiltonian assuming the usual statistical mechanical correspondence seems to be feasible, and in fact, a great deal of work along these lines has already been done. ⁴ In Sec. II we state precisely what we mean by

analyticity of a thermodynamic potential in the neighborhood of a critical point, and show the relationship to van der Waals continuity of states.² For simplicity, this will be done in magnetic language using the Weiss or molecular field theory. This will be presented in a manner which we believe has not been seen before and which proves to be very illuminating.

Section II leads to an immediate generalization of the form of the thermodynamic potential which we present in Sec. III. The generalization is restricted to those thermodynamic potentials which give rational critical exponents, but the sets of critical exponents include those which are not necessarily equal above and below the critical point nor on either side of the coexistence curve. These functions include the homogeneous functions of Widom' with rational critical exponents as a special case. It is shown that the equality sign in Rushbrooke's inequality' holds as a consequence of the symmetry of the coexistence curve about the critical point, so that the scaling law, α' +2 β + γ' = 2, is independent of the particular choice of function for magnetic systems, and hence independent of the form of the interaction. Symmetry of the coexistence curve does not guarantee the equality sign in the other known inequalities, however, so that equality holds only for particular choices of thermodynamic potentials. Finally, it is shown that the scaling laws can be generalized to include critical exponents of derivatives of the thermodynamic potential higher than the second.

In Sec. IV we present some specific examples of the general class of functions given in Sec. III. These are of value in elucidating the various "schemes" which have been proposed, as well as putting them in proper perspective relative to the present analysis. Most of these schemes have already been cited by Griffiths,¹ but it is interesting to see how the concept of algebraic

functions, besides being a powerful analytic tool, simplifies and unifies the practical procedure of finding examples of thermodynamic potentials.

II. ANALYTIC FUNCTIONS OF SEVERAL VARIABLES

One of the great developments of the nineteenth century was the invention of the complex plane and the notion of analyticity of a function in one variable. The twentieth century saw the extension of this concept to more than one variable with a number of surprising theorems appearing, which pointed up a fundamental difference between one variable and several. One of the most important for our present purpose is the theorem that all isolated singularities of an analytic function of more than one variable are removable.⁷ An important corollary is that singularities must have trajectories in the Cartesian product space of the several variables. The example of Regge poles is familiar in S-matrix theory, but the fact seems to have been overlooked as far as thermodynamics is concerned. This theorem is, of course, not true for one variable. A simple application of this theorem yields the result that (a) the critical point alone cannot be an isolated singularity, and (b) the coexistence curve alone cannot represent a line of singularities. In both cases, there must be other singularities in the complex manifold defined by whatever thermodynamic variables we are concerned with.

Now, one of the characteristics of a critical point is, as noted by van der Waals, the apparent continuity of liquid and vapor states above the critical temperature. If we replace the word "continuity" by "analyticity", then what we are postulating is the analytic continuation of, say, the Helmholtz free energy in both its natural variables for all values of these variables. Note that this is not the same as the situation in the van der Waals theory, where the pressure can be analytically continued in the density alone for all values of the temperature. Whether the true thermodynamic potential can or cannot be analytically continued in any one of its variables is an irrelevant question. The physics of the situation dictates analytic continuation in all its variables together, if we are to assume analytic continuation at all. Thus, we replace Griffiths' postulates 5 and 6 by the single equivalent statement¹: In the neighborhood of a critical point, any thermodynamic potential used to describe the system is a holomorphic function of all its natural variables with singularities (at least) on the coexistence curve and at the critical point. The physical states of the system correspond to the smallest real values of this thermodynamic potential for real values of its variables (minimum principle) with the added proviso that all the derivatives be real. In the language of Smatrix theory, the physical values of the thermodynamic potential are its boundary values on the real axis. As we will make clear in an example, it is not necessary to postulate the particular

analytic behavior of the coexistence curve itself. This will follow naturally from the above statement. We must also keep Griffiths' postulates 1, 3 and 4, which are the ordinary postulates of thermodynamics.⁸ His postulate 2, however, need not be kept, since, as we shall see, it is contained in the minimum principle.

The example which we choose to illustrate the foregoing general postulate is the so-called classical theory of a critical point as exemplified by the van der Waals equation of state or the Weiss (molecular) field theory of ferromagnetism. For simplicity, we shall use the magnetic language. In the molecular field theory, the magnetic free energy per spin is given by'

$$
A(M, T) = \frac{1}{2}kT\ln(1 - M^2) + \frac{1}{2}MkT\ln\left(\frac{1 + M}{1 - M}\right)
$$

 $-\frac{1}{2}JM^2 - kT\ln 2$ (1)

with the entropy per spin and magnetic field given by

$$
S = -(\partial A/\partial T)_{M}; \quad H = (\partial A/\partial M)_{T}.
$$
 (2)

In these, as in all subsequent equations, N is the number of spins, M is the average magnetization per spin, H is the applied field and J is the value of the exchange integral. The symbols k and T have their usual meaning of Boltzmann's constant and temperature, respectively. The second of Eqs. (2) yields the well known subsidiary condition

$$
\tanh[(H+JM)/kT] = M \tag{3}
$$

where the magnetic moment per spin has been set equal to unity. When Eq. (3) is used to eliminate H in Eq. (1), the isotherms of A/N are seen to be those schematically shown in Fig. 1. For $T < T_c$, the physical values of A must be obtained by the "double-tangent" construction, which determines the coexistence curve or curve of spontaneous magnetization. The region inside the coexistence curve represents an unphysical or forbidden region for the

FIG. 1. Molecular-field theory isotherms for A(M, 7}. The dashed line represents the double tangent eonstruetion.

magnetization variable. From the mathematical point of view this is somewhat unsatisfactory, since we now have a function which is undefined for certain values of the variables. To remedy this, we look at the Legendre transform of $A(M, T)$ with respect to M. This will be denoted by $F(H, T)$ and has the properties that

$$
S = -(\partial F/\partial T)_H; \quad M = -(\partial F/\partial H)_T \quad (4)
$$

It is readily seen that the isotherms of F are given schematically by Fig. 2. Thus, the coexgiven schematically by Fig. 2. Thus, the $\mathfrak c$
istence curve has been "closed up, " and the function is defined for all values of the variables in the neighborhood of the critical point. In the case of the molecular field theory, it appears that one must pay the price of having a triple valued function, but we shall see that it is just this multiple valuedness which provides a means of representing the function most conveniently in the neighborhood of the critical point. We first note that our single postulate immediately determines the physical values of $F(H, T)$. These are simply the values shown by the solid lines of Fig. 2.

FIG. 2. Molecular-field theory isotherms for F(H, T). The dashed portion of the curve represents the unphysical region. The isolated point is the acnode for $T>T_c$.

We now inquire into the means of representing the function shown in Fig. 2. We mention in passing that this type of behavior has already
been observed in analytic S-matrix theory,¹⁰ been observed in analytic S-matrix theory, and is described by the Jaberwockian statement that when two cusps come together in the neighborhood of a crunode, the curve changes into a continuous curve plus an acnode. In the molecular field theory the acnode is actually present, as can be seen by taking M and H to be pure imaginary. Equation (8) then becomes

$$
\tan[(H+JM)/kT]=M,\tag{5}
$$

since $J=kT_c$. Equation (5) has the single solution $M = O$ for $H = O$ when $T < T_c$, and multiple

solutions for $H = O$ when $T > T_c$. Thus, the molecular field theory has a spontaneous imaginary magnetization above the critical temperature. Since $F(H, T)$ is real for $H = O$, this gives an isolated real point which is the acnode. (Actually, there is an infinite series of acnodes, which do not converge as the critical point is approached. Since we are only interested in a neighborhood of the critical point, we shall ignore these in this paper.) Returning to Fig. 2, we see that the isotherms of $F(H, T)$ have three branches and two branch points (two cusps and a crunode or acnode) in the neighborhood of the critical point. Such a curve is an algebraic curve and is described by an algebraic function. Recalling that an algebraic function $f(z)$ with *n* branches is defined by the equation

$$
P(f, z) = a_0(z)f^n + a_1(z)f^{n-1} + \cdots
$$

+ a_n(z) = 0, (6)

where $P(f, z)$ is an irreducible polynomial in f and z, and the coefficients $a_{\gamma}(z)$ are polynomials in the variable z , we find by straightforward but tedious computation that the molecular-field free energy satisfies the equation

$$
f^3 + \frac{3}{2}t^2f^2 + \left(\frac{9}{16}t^4 + \frac{27}{8}z^2t\right)f + \frac{81}{64}z^4 + \frac{9}{32}z^2t^3 = 0, \qquad (7)
$$

where $f = F + kT \ln 2$, $z = H$, and $t = (T - T_c)/T_c$ enters as a parameter. We now observe that Eq. (7) defines an algebraic function of the two variables z and t . Since, by definition, all branches of an algebraic function are analytic continuations of each other (albeit in both variables), we see that the function defined by Eq. (7) demonstrates van der Waals' continuity of states, i. e. analytic continuation of states. We also notice that, although the polynomial of Eq. (7) is formally irreducible, nevertheless, for a particular value of z ($z = 0$), the polynomial regarded as a function of t alone is, in fact, reducible. This means that the coexistence curve consists of two pieces which are not analytic continuations of each other, although each piece separately has an analytic continuation. These two pieces are given by

$$
f=0 \text{ for } t>0,
$$
 (8a)

$$
f = -\frac{3}{4}t^2
$$
 for $t < 0$. (8b)

The fact that the function of Eq. (8b) happens to be analytic at $t = 0$ is a mathematical accident of the molecular-field and van der Waals theories, and has led to a great deal of confusion and speculation on the analytic behavior of thermodynamic functions at the critical point. The situation, however, is quite clear when looked at in the present light. The physical free energy, as given by Eqs. (8a) and (8b) together, is always singular at the critical point, even for the apparently mell-behaved classical theory. Thus, the classical theory as exemplified by

the molecular-field free energy is no more nor less analytic than any more general free energy, and is (by way of an accident) the simplest special case of the general functions which will
be presented in the next section.¹¹ be presented in the next section.

III. GENERAL FORM OF THERMODYNAMIC **POTENTIALS**

With the example of Sec. II in mind, we now show how to construct the most general algebraic function which represents the magneticfield free energy F in the neighborhood of the Curie point. This function can then be used to investigate the proposed theorems involving critical exponents, the so-called scaling laws.

In order to construct the most general algebraic function representing the free energy, it is first necessary to describe its boundary (real) values on the real axes. These constitute the physical values of the function. (Although it is tempting to refer to that part of the Riemann surface on which the function is real as the physical sheet, this would not be analogous to the situation in S-matrix theory where the appropriate part of the Riemann surface on the entire complex energy plane is so referred to. } The boundary values are easily described by fixing each of the variables separately and making use of the convexity conditions,

$$
\left(\frac{\partial^2 F}{\partial T^2}\right)_H = \frac{C_H}{T} < 0,
$$
\n(9a)

$$
\left(\frac{\partial^2 F}{\partial H^2}\right)_T = -\chi < 0,\tag{9b}
$$

and
$$
\left(\frac{\partial^2 F}{\partial H^2}\right)_T \left(\frac{\partial^2 F}{\partial T^2}\right)_H - \left(\frac{\partial^2 F}{\partial H^2 T}\right)^2 > 0.
$$
 (9c)

Thus, the two families of curves, F vs. ReH and F vs. Ret are convex upwards. (Note that since F is defined for all values of H and t in a neighborhood of the origin, we can use the convexity conditions Eqs. $(9a)-(9c)$ as they stand without having to. resort to a tangent definition of convexity.) However, the condition which characterizes a critical point is that the first derivative of F, $(\partial F/\partial H)_t$, is double valued at $H=0$ for values of t less than zero. A more physical way of saying this, is that, for values of t less than zero, there exist metastable states of the system which may be given by analytic continuation of each phase (a phase being defined as the state of the system for either positive or negative values of H). Thus, the family of curves of F vs. ReH exhibits a crunode at $H = 0$ for values of t less than zero. It is this crunode which constitutes the essential feature of a phase transition with a critical point, and which enables us to characterize the free energy in terms of algebraic functions.

We now examine the polynomial which defines the algebraic function representing the free energy. We subtract the appropriate non-

singular part of the free energy from $F(H, T)$ to form the function $F^*(H, t)$, which is zero at $H=t=0$. (In the molecular field theory this nonsingular part is $-kTln2$. Because the free energy has a crunode at $H=0$ for t less than zero, the function F^* is double valued there. Denoting the defining polynomial by $P(F^*;H, t)$ and dropping the asterisk, we see that it must be of the following form when $H = 0$:

$$
P(F; 0, t) = R_2^{2}(F, t)R_{1}(F, t)Q_{1}(F, t)
$$
 (10)

where R denotes a polynomial which has at least one real root and Q denotes a polynomial which has no real roots smaller than those of the R 's. The minus and plus signs on the polynomials R in Eq. (10) indicate that the roots determine the branches of F representing the free energy for negative and positive values of t, respectively. The polynomial $R_$ is squared to show explicitly the double real root (crunode) at $H = 0$. As an example, we again quote the molecular field result where $P(F; 0, t)$ is given by

$$
P(F, 0, t) = F^3 + \frac{3}{2}t^2F^2 + \frac{9}{16}t^4F = (F + \frac{3}{4}t^2)^2F. \quad (11)
$$

For this case, we have $R = F + \frac{3}{4}t^2$, $R_+ = F$, and $Q_1 = 1$. Thus, the equation $P(F; 0, t) = 0$ has the roots $F=-\frac{3}{4}t^2$ and $F=0$, which determine the free energy for negative and positive t , respectively, on the coexistence curve $H=0$. The critical isotherm contains less information. For the magnetic case, it is symmetric in H . Therefore, $P(F; H, 0)$ can be written either as

$$
P(F; H, 0) = R_1(F, H^2) Q_2(F, H^2), \qquad (12a)
$$

or
$$
P(F; H, 0) = R_2(F, H)R_2(F, -H)Q_2(F, H^2)
$$
, (12b)

where R and Q again denote polynomials with at least one real root and no smaller real roots, respectively. The molecular field theory illustrates the first form (12a) where \mathbf{L}

$$
R_1 = F_3 + \frac{81}{24}H^4,\tag{13}
$$

so that the critical isotherm is given by F $=-\frac{3}{4}3^{1/3}H^{4/3}$. The second form is more interesting, however. It shows that, even though the critical isotherm is symmetric, the exponent governing the behavior of F with respect to H need not necessarily have an even numerator An example is

$$
R_2(F, H) = F^4 + H^5 \tag{14a}
$$

$$
R_2(F, H) = F^4 + H^5
$$
 (14a)

$$
R_2(F, -H) = F^4 - H^5
$$
 (14b)

$$
Q_2 = 1. \tag{14c}
$$

Putting $P(F; H, 0) = 0$, we get two distinct odd functions of H which, like the coexistence curve of the molecular field theory, are not analytically continuable into each other in H . The minimum principle guarantees that we take the smaller real value, however, so that the physical values of the free energy form an even function in H given by $F = -\left| \widetilde{H} \right|^{5/4}$.

Equations (10) and (12) constitute a general representation of the boundary conditions on the real axes for the function F , with the added proviso that it be convex upward in both variables. The most general algebraic function can now be found by writing down a polynomial $P(F; H, t)$ which reduces to the form of Eqs. (10) and (12) for $H = 0$ and $t = 0$, respectively. Although this cannot be done explicitly, nevertheless, we can draw some important conclusions with regard to the scaling laws from the forms of the boundary conditions. (We can, of course, give particular forms for the polynomial P which are equivalent to the various schemes extant, and which are also useful in analyzing experiand which are also useful in analyzing experiental data.¹² This will be done in the next section.) In order to find the consequences of Eqs. (10) and (12), we try to find those aspects of the free energy which are invariant with respect to the choice of function. To do this, we examine the critical exponents which are determined by these functions. In the neighborhood of a singular point, an algebraic function of one variable can be expanded in the following way.¹³

$$
f(z) = \sum_{j=\gamma}^{\infty} a_j \zeta^j,
$$
 (15)

where $\zeta = z^{1/n}$, *n* is the degree of the algebraic function (degree of the defining polynomial), and r is a positive or negative integer. In the present case, the critical point is a singular point in both variables, whereas the critical curves are singular in only one of the variables. Therefore, the free energy can be expanded about a point (not the critical point) on either the coexistence curve $(H = 0)$ or the critical isotherm $(t=0)$ as follows:

$$
F = a(t) + b(t)H + c(t)H^2 + \cdots, \qquad (16a)
$$

$$
\text{or} \quad F = d(H) + e(H)t + f(H)t^2 + \cdots, \tag{16b}
$$

where the coefficients a to f have the form given by Eq. (15). The leading term of each coefficient $(i = r)$ determines the critical exponent for the corresponding power of H or t which represents a particular thermodynamic quantity. For example, using Eqs. $(16a)$ and $(16b)$ and standard thermodynamic notation, we have

$$
C_{H=0} = -Ta^{\prime\prime}(t),\tag{17a}
$$

$$
M(t) \equiv M(t, H = 0) = -b(t),
$$
 (17b)

$$
\chi \equiv \chi(t, H=0) = -2c(t), \qquad (17c)
$$

$$
M(H) \equiv M(t = 0, H) = -d'(H),
$$
 (17d)

$$
S(H) \equiv S(t=0, H) = -e(H), \qquad (17e)
$$

$$
C_H \equiv C_H(t=0) = -2T_c f(H). \tag{17f}
$$

The coefficients themselves are determined by inserting Eqs. $(16a)$ and $(16b)$ into the defining equation for F and equating the coefficients of

equal powers of H or t . Using the molecular field theory [Eq. (7)] as an example again, we find the following set of equations for the coefficients ^a to f.

$$
a^3 + \frac{3}{2}t^2a^2 + \frac{9}{16}t^4a = 0
$$
 (18a)

$$
3a^2b + 3t^2ab + \frac{9}{16}t^4b = 0
$$
 (18b)

 $3ab^2+3a^2c+\frac{3}{2}t^2b^2+3t^2ac$

$$
+\frac{9}{16}t^4c + \frac{27}{8}ta + \frac{9}{32}t^3 = 0
$$
 (18c)

$$
b^3+6ab^2c+3a^2g+3t^2bc
$$

$$
+3ta^2g+\frac{9}{16}t^4g+\frac{27}{8}tb=0
$$
 (18d)

$$
d^3 + \frac{81}{64}H^4 = 0 \tag{19a}
$$

$$
3d^2e + \frac{27}{8}H^2d = 0
$$
 (19b)

$$
3de^2 + 3d^2f + \frac{3}{2}d^2 + \frac{27}{8}H^2e = 0
$$
 (19c)

where g is the coefficient of the H^3 term in Eq. $(16a)$. The need for Eq. $(18d)$ will become apparent when we solve for the coefficients. The solutions of Eqs. (18) fall into two categories depending on the branch of the algebraic function we wish to be on. We shall denote by a sub $script + or - the coefficients referring to the$ branch of the algebraic function which determines the free energy for positive or negative t , respectively. For positive t , the solutions of Eqs. $(18a) - (18c)$ are

$$
a_{\parallel} = 0, \tag{20a}
$$

$$
b_{\perp} = 0, \tag{20b}
$$

$$
c_{+} = -\frac{1}{2}t^{-1}.
$$
 (20c)

For negative t, the solution to Eq. (18a) for $a_$ makes the coefficient of $b_$ in Eq. (18b) zero, so that this equation becomes an identity. The coefficient b_- is then determined from Eq. (18c), where the coefficient of c_{-} is seen to be zero, while c_- must be determined from Eq. (18d), where the coefficient of g vanishes. The results are

$$
a_{-} = -\frac{3}{4}(-t)^2, \tag{21a}
$$

$$
b_{-} = \pm 3^{\frac{1}{2}} (-t)^{\frac{1}{2}},
$$
 (21b)

$$
c_{-} = -\frac{1}{4}(-t)^{-1}.
$$
 (21c)

From Eqs. (19) we get

$$
d = -(3^{4/3}/4)H^{4/3}, \qquad (22a)
$$

$$
e = (3^{2/3}/2)H^{2/3}, \qquad (22b)
$$

$$
f = -\frac{1}{2} \tag{22c}
$$

The behavior exhibited in computing the coefficients $a_-, b_-,$ and c_- (having to use the next recurrence relation because the second one

vanishes identically) is symptomatic of the most general function, and leads at once to a theorem concerning the inequality first derived by Rushbrooke. Before stating the theorem, we first note that the function $\widetilde{F}(H, t)$ will be homogeneous in $H^{\hat{D}}$ and $t^{\hat{q}}$, if and only if the defining polynomial $P(F; H, t)$ is homogeneous in F, H^p , and t^q . (This follows directly from the definition of homogeneity.) For the molecular field theory $p = \frac{4}{3}$ and $q = 2$, and the degree of homogeneity of the defining polynomial is 3. The coefficients can be computed formally by observing that the following relations hold:

$$
a_{\pm}(t) = F(H, t) |_{H=0,}
$$
 (23a)

$$
b_{\pm}(t) = \partial F(H, t) / \partial H|_{H=0},
$$
\n(23b)

$$
c_{\pm}(t) = \frac{1}{2} \partial^2 F(H, t) / \partial H^2|_{H^2(0)},
$$
 (23c)

and $d(H) = F(H, t) \Big|_{t=0}$, (24a)

$$
e(H) = \partial F(H, t) / \partial t \vert_{t=0}, \qquad (24b)
$$

$$
f(H) = \frac{1}{2} \partial^2 F(H, t) / \partial t^2 \Big|_{t=0} .
$$
 (24c)

Consequently, the coefficients are solutions to the set of equations given by

$$
\left.\partial^{\hat{i}}P(F;H,t)/\partial H^{\hat{i}}\right|_{H^2=0}=0\tag{25}
$$

and
$$
\partial^i P(F; H, t) / \partial t^i \rvert_{t=0} = 0
$$
 (26)

where $i = 1, 2, 3, \ldots$ and F is regarded as a function of H and t. Equations (25) and (26) become Eqs. (18) and (19) for the molecular field theory. If we first generalize to homogeneous free energies, then the defining polynomial P will be homogeneous and so will all the P_n 's. As a result, the leading exponent governing the behavior of the coefficients a to f will not depend on which branch the algebraic function $F(H, t)$ is being expanded on. Therefore, the exponents governing the behaviors of a_+ and a_- will be equal, as well as the exponents governing the behaviors of c_+ and c_- . (The coefficient b_+ is always identically zero, so that its exponent is undefined.) Moreover, only two of the exponents can be chosen independently. This can be seen by computing the exponents from Eqs. (25) and (26). Since these equations are homogeneous, the exponent governirg the behavior of the appropriate coefficient can be obtained by examining the first term of $P_i(F; H, t)$ which is proportional to F^{n-i} . First note that

$$
\partial P(F; H, t)/\partial H|_{H=0}
$$

= $[2R_{-}(F, t)(\partial R_{-}/\partial F)R_{+}(F, t)Q_{1}(F, t) + R_{-}^{2}(F, t)(\partial R_{+}/\partial F)Q_{1}(F, t) + R_{-}^{2}(F, t)R_{+}(F, t)(\partial Q_{1}/\partial F)]\frac{\partial F}{\partial H}(H, t)|_{H=0}$

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$$
= \partial P(F; H = 0, t) / \partial F|_{F = a} b = 0 \tag{27}
$$

which is identically zero on the branch of the function F , which determines its behavior for negative t , since a ₋ satisfies the equation regative *i*, since u_{-} satisfies the equation
 $R_{-}(a_{-}, t) = 0$. Hence, $\partial F(H, t)/\partial H|_{H=0} = b_{-}$ is undetermined from Eq. (27) , and we must look at the next equation in the set. This is

$$
\frac{\partial^2 P(F; H, t)}{\partial H^2} \Big|_{H=0}
$$
\n
$$
= \frac{\partial P(F; H=0, t)}{\partial F} \Big|_{F=a} \frac{\partial^2 F(H, t)}{\partial H^2} \Big|_{H=0}
$$
\n
$$
+ \frac{\partial^2 P(F; H=0, t)}{\partial F^2} \Big|_{F=a} \Big(\frac{\partial F(H, t)}{\partial H} \Big)^2 \Big|_{H=0}
$$
\n
$$
+ 2P_2(F, t) = \frac{\partial P(F; H=0, t)}{\partial F} \Big|_{F=a} c
$$
\n
$$
+ \frac{\partial^2 P(F; H=0, t)}{\partial F^2} \Big|_{F=a} b^2 + 2P_2(F, t) = 0, \qquad (28)
$$

where $P_{2}(F, t)$ is the (polynomial) coefficient of H^2 in $P(\tilde{F}; H, t)$. As in Eq. (27), the coefficient H^2 in $P(F; H, t)$. As in Eq. (27), the coefficien
of c_{-2} , $\partial P(F; H=0, t)/\partial F|_{F_1=a_2}$ vanishes on the branch which determines the free energy for negative t. Thus $b_$ is independent of $a_$, since $P_2(F, t)$ can be chosen independently of $P(F; H=0, 0)$ t). The next recurrence relation shows that c_{-} is not independent of a_+ and b_- . We have

$$
\frac{\partial^3 P(F; H, t)}{\partial H^3} \Big|_{H=0}
$$

=\frac{\partial P(F; H=0, t)}{\partial F} \Big|_{F=a} g + 3 \frac{\partial^2 P(F; H=0, t)}{\partial F^2} \Big|_{F=a} b c
+ 2 \frac{\partial P_2(F, t)}{\partial F} \Big|_{F=a} b + \frac{\partial^3 P(F; H=0, t)}{\partial F^3} \Big|_{F=a} b^3 = 0. (29)

Again, the first coefficient vanishes on the branch determined by negative t , so that c . is determined from the equation

$$
3\frac{\partial^2 P(F; H = 0, t)}{\partial F^2} \Big|_{\substack{F = a_-}} F = a_- \Big|_{\substack{a_+ \text{odd } b_+}} F = a_- \Big|_{\substack{h_+ \text{odd } b_+}} \tag{30}
$$

Since $P(F; H, t)$ is homogeneous, all the polynomials in Eq. (30) are homogeneous and of the same degree. Therefore, it is sufficient to look at the term which arises from $F^{\bar{n}}$ in $P(F;$ H, t). This contributes to the coefficients of c and $b_{}$ ² in Eq. (30). The two relevant terms are

 $2n(n-1)a_n - 2c_n$ and $n(n-1)(n-2)a_n - 3b_n$ and we immediately get

$$
a_{-}c_{-}^{\sim}b_{-}^{2}.
$$
 (31)

Using Fisher's notation,

$$
a_+(t) \sim t^{2-\alpha}, \tag{32a}
$$

$$
a_{-}(t) \sim (-t)^{2-\alpha'}, \tag{32b}
$$

$$
b_{-}(t) \sim (-t)^{\beta} \tag{32c}
$$

$$
c_{+}(t) \sim t^{-\gamma} \tag{32d}
$$

$$
c_{-}(t) \sim (-t)^{-\gamma'}, \tag{32e}
$$

we find α' +2 β + γ' =2. Similarly, for the coefficients governing the behavior of F along the critical isotherm, we have

$$
P(d; H, t = 0) = 0,
$$
 (33a)

$$
\frac{\partial P(F; H, t)}{\partial t}\Big|_{t=0} = \frac{\partial P(F; H, t=0)}{\partial F}\Big|_{F=d} e
$$

+ $\Pi_1(d, H) = 0$, (33b)

$$
\frac{\partial^2 P(F; H, t)}{\partial t^2} \Big|_{t=0} = \frac{\partial^2 P(F; H, t=0)}{\partial F^2} \Big|_{F=d} e^{2}
$$

$$
+ \frac{\partial P(F; H, t=0)}{\partial F} \Big|_{F=d} f + \frac{\partial \Pi_1(F, H)}{\partial F} \Big|_{F=d} e
$$

$$
+ \Pi_2(d, H) = 0 , \qquad (33c)
$$

where Π_1 and Π_2 are the (polynomial) coefficients of t and \bar{t}^2 in $P(F; H, t)$. It is evident from Eqs. (28), (30), and (33) that if $P(F; H, t)$ is homogeneous of degree n in F , $H^{\!\mathcal{P}}$, and $t\,q$, then the critical exponents will be given by

$$
\alpha = \alpha' = 2 - q \tag{34a}
$$

$$
\beta = q(p-1)/p \quad , \tag{34b}
$$

$$
\gamma = \gamma' = q(2-p)/p, \tag{34c}
$$

$$
\delta = 1/(\rho - 1) \tag{34d}
$$

$$
\epsilon = p(q-1)/q, \qquad (34e)
$$

$$
\phi = p(2-q)/q \tag{34f}
$$

where δ , ϵ , and ϕ are defined by

$$
d(H) \sim |H|^{1+1/\delta}, \tag{35a}
$$

$$
e(H) \sim |H|^\epsilon \tag{35b}
$$

$$
f(H) \sim |H|^{-\phi}.
$$
 (35c)

Equations (34a) to (34f) constitute the scaling laws of Kadanoff¹⁴ and, in fact, the quantities p and q represent the two independent scaling parameters. Upon elimination of these two scaling parameters, one finds relations among any three of the six exponents given by Eqs. $(34a)$ - $(34f)$. Only four of these relations are independent, however. They can be written as

$$
\alpha' + 2\beta + \gamma' = 2, \qquad (36a)
$$

$$
2\epsilon + \phi - 1/\delta = 1, \qquad (36b)
$$

$$
\alpha' + \beta(\delta + 1) = 2, \qquad (36c)
$$

$$
\epsilon (2 - \alpha') / (1 - \alpha') - \delta^{-1} = 1.
$$
 (36d)

Thermodynamic inequalities which reduce to the equalities of Eqs. (36a)–(36d) have already
been derived.^{6,15,16} (Note that the critical exponent ζ defined by Griffiths is equal to $\epsilon \delta - 1$. We have just seen that the assumption of homogeneity is a sufficient condition for the equality sign or scaling laws to hold. It is not a necessary condition, however. Consequently, the remainder of this section will be devoted to the determination of the (weaker) conditions under which some or all of Eqs. $(36a)$ - $(36d)$ will hold. In the future, we shall refer to these equations, rather than Eqs. $(34a)$ - $(34f)$ as scaling laws. Examining the previous demonstration of Eq. (36a), we shall show that it is not necessary to assume homogeneity in order for the argument to be valid. Indeed, it is a direct consequence of the fact that there is no H^3 term in $P(F; H, t)$, which is due to the fact that the magnetic free energy is symmetric in H . To see this, we again examine Eqs. (28) and (30) which determine $b_$ and c_{-} . Since b_{-} is determined by the magnitude of $P_2(F = a_-, t)$, the last two terms on the left hand side of $Eq.$ (30) will be of the same order of magnitude in t and this order of magnitude of magnitude in *t* and this order of magnitude
is given by the order of magnitude of $a_+^{-1} \times$ $\left[\partial^2 P(F; H=0, t)/\partial F^2\right]_{F=a} b_+^2$. The reason is that the terms of lowest order (largest size) in t in the polynomial $P(F; H = 0, t)$ must include a term of the form $F^{\gamma}t^s$ where $r \ge 4$. This follows from the form of $P(F; 0, t)$ given by Eq. (10) and the fact that $a_$ is a root of this polynomial. As before with the term F^n , the term F^{γ} contribbefore with the term $\frac{1}{n}$, the term $\frac{1}{n}$ contributes to the coefficients of c_- and b_-^2 in Eq. (30).
The relevant terms are $2r(r-1)a_-^2$ $r^2b_+^sc_-$ and $r(r-1)(r-2)a$ ^{r-3} t^sb ², so that Eq. (31) again holds. We have therefore shown that the scaling law of Eq. (36a) holds as a consequence of symmetry of the free energy in the applied field, when the critical behavior of thermodynamic functions is given by power series expansions of the type of Eq. (15) with rational exponents. If, for example, the three dimensional Ising model could be shown to have such expansions for its free energy, then the equality sign would be guaranteed in Rushbrooke's inequality. (The two dimensional Ising model is excluded from the present discussion because of the logarithmic singularity in C_H .) Unfortunately, the other scaling laws are not consequences of such simple considerations. However, by extending the concept of critical exponent to the behavior of derivatives of the free energy

higher than the second, we can find relations similar to Eq. (36a). These relations may be referred to as super scaling laws to distinguish them from the scaling laws of Eqs. (36). In order to find them, we first establish a more convenient notation for the expansion of the free energy on the coexistence curve and critical isotherm. Corresponding to Eqs. (16a) and (16b) we write

$$
F = \sum_{i=0}^{\infty} a_i(t) H^i
$$
 (37a)

$$
\text{or} \quad F = \sum_{i=0}^{\infty} b_i(H)t^i,
$$
 (37b)

where the coefficients a_i and b_i again have the form given by Eq. (15). The exponent of the leading term, which is the critical exponent, will be denoted by α or β , so that we have

$$
a_i^{\ \ +}(t) \sim t^{\alpha_i^{\ \ +}} \quad , \tag{38a}
$$

$$
a_i^-(t) \sim (-t)^{\alpha_i}, \qquad (38b)
$$

$$
b_i(H) \sim |H|^{2i}, \qquad (38c) \qquad a_i^- a_i^- \sim a_3^- a_2^- \qquad (43)
$$

where the $+$ and $-$ signs have the same meaning as before. The relationship to the previous notation is obvious. We now compute these critical exponents using the recursion relations of Eqs. (25) and (26) . We have already seen that the presence of a term of the form $P_{\gamma}(F, t)H^{\gamma}$ in $P(F; H, t)$ determines the order of magnitude of the coefficient $a_{\gamma-1}^-(t)$ when $\gamma=0$, 1, 2. It is evident that this is true in general. When the term is absent, however, as in the magnetic case when r is odd, the order of magnitude of the corresponding coefficient is then determined by the coefficients with smaller subscripts. Examination of the recursion relations (25) for $i = 4$, 5 will show how this works in general. We have

$$
\frac{\partial^4 P(F; H, t)}{\partial H^4} \Big|_{H=0} = \frac{\partial P(F; 0, t)}{\partial F} \Big|_{F=a_0} a_4
$$

+
$$
\frac{\partial^2 P(F; 0, t)}{\partial F^2} \Big|_{F=a_0} (4a_3a_1 + 3a_2^2)
$$

+
$$
\frac{\partial^3 P(F; 0, t)}{\partial F^3} \Big|_{F=a_0} a_2a_1^2 + \frac{\partial^4 P(F; 0, t)}{\partial F^4} \Big|_{F=a_0} a_1^4
$$

+
$$
2 \frac{\partial^2 P_2(F, t)}{\partial F^2} \Big|_{F=a_0} a_1^2 + 24P_4(a_0, t) = 0
$$
 (39)

and
$$
\frac{\left.\frac{\partial^5 P(F; H, t)}{\partial H^5}\right|_{H=0} = \frac{\left.\frac{\partial P(F; 0, t)}{\partial F}\right|_{F=a_0} a_t}{\left.\frac{\partial^2 P(F; 0, t)}{\partial F^2}\right|_{F=a_0}}
$$

 $\sin(\pi, \alpha, \Lambda)$

$$
\begin{array}{ll}\n\text{s} & +\frac{\partial^3 P(F; 0, t)}{\partial F^3} \Big|_{F = a_0} \quad (10a_3a_1^2 + 15a_2^2a_1) \\
\text{with} \\
\text{is} \\
\text{if } e \\
\text{if } e \\
\text{if } e \\
\text{if } e \\
\text{if } e\n\end{array}\n\quad\n\begin{array}{ll}\n\text{if } 10a_3a_1^2 + 15a_2^2a_1 \\
\text{if } e \\
\text{if } e \\
\text{if } e \\
\text{if } e\n\end{array}
$$
\n
$$
\begin{array}{ll}\n\text{if } e \\
\text{if } 10^{\frac{\partial^4 P(F; 0, t)}{\partial F^4}} \Big|_{F = a_0} a_2a_1^3 \\
\text{if } e \\
\text{if } e \\
\text{if } e \\
\text{if } e \\
\text{if } e\n\end{array}
$$
\n
$$
\begin{array}{ll}\n\text{if } 10a_3a_1^2 + 15a_2^2a_1 \\
\text{if } e \\
\text{if } e \\
\text{if } e \\
\text{if } e\n\end{array}
$$
\n
$$
\begin{array}{ll}\n\text{if } 10a_3a_1^2 + 15a_2^2a_1 \\
\text{if } e \\
\text{if } e \\
\text{if } e \\
\text{if } e\n\end{array}
$$
\n
$$
\begin{array}{ll}\n\text{if } 10a_3a_1^2 + 15a_2^2a_1 \\
\text{if } e \\
\text{if } e \\
\text{if } e \\
\text{if } e\n\end{array}
$$
\n
$$
\begin{array}{ll}\n\text{if } 10a_3a_1^2 + 15a_2^2a_1 \\
\text{if } e \\
\text{if } e \\
\text{if } e \\
\text{if } e\n\end{array}
$$
\n
$$
\begin{array}{ll}\n\text{if } 10a_3a_1^2 + 15a_2^2a_1 \\
\text{if } e \\
\text{if } e \\
\text{if } e\n\end{array}
$$
\n
$$
\begin{array}{ll}\n\text{if } 10a_3a_1^2 + 15a_2^2a_1 \\
\text{if } e \\
\text{if } e \\
\text{if } e \\
$$

When $F = a_0^-$, the first term on the right hand side of Eqs. (38) and (40) vanishes. The magnitude of a_3 ⁻ is determined by $P_4(a_0^-, t)$ when it is the term of lowest order in Eq. (38) . We therefore get

$$
a_3^{\text{--}} a_1^{\text{--}} \ge (a_2^{\text{--}})^2 \tag{41}
$$

or
$$
\alpha_1^{\text{--}} - 2\alpha_2^{\text{--}} + \alpha_3^{\text{--}} \leq 0.
$$
 (42)

However, since $P_5(a_0^-, t) = 0$, the magnitude of a_4 ⁻ is determined in Eq. (40) by the previous a^{\dagger} s and we get

$$
a_4^{} a_1^{} \sim a_3^{} a_2^{} \tag{43}
$$

or
$$
\alpha_1 - \alpha_2 - \alpha_3 - \alpha_4 = 0.
$$
 (44)

In general, we have

$$
\alpha_1 - \alpha_2 - \alpha_{n-1} + \alpha_n \le 0; n = 3, 5, ...,
$$

= 0; n = 4, 6, ..., (45a)

or, since
$$
\alpha_0 - 2\alpha_1 + \alpha_2 = 0
$$
,
\n
$$
\alpha_0 - \alpha_1 - \alpha_{n-1} + \alpha_n \leq 0; \quad n = 3, 5, \dots,
$$
\n
$$
= 0; \quad n = 2, 4, \dots
$$
\n(45b)

We shall refer to equations of the type of Eq. (45) as super scaling laws when the equality sign holds. They are implied (but do not imply) the equalities given by Essam and Fisher¹⁷ for homogeneous functions. For large n , the presence or absence of the equality sign becomes a moot point, but for small n verification of the super scaling laws is within the realm of possibility. For example, Kouvel and Rodbell¹⁸ have alread measured α_4^+ for nickel and CrO₂, and Baker
et al.¹⁹ have made numerical calculations of α et al.¹⁹ have made numerical calculations of α_n for $n = 4, 6, 8$ for the Heisenberg model. There has also been some discussion of these higher exponents more recently by Fisher,²⁰ who refers to the difference $\alpha_n - \alpha_{n-1} = \Delta$ as the "gap exponent."

nent."
For the α^{+} 's and β 's, symmetry of the free energy in H does not guarantee the equality sign in relations of the type of Eq. (45). Since a_n is determined by the nth recursion relation rather than the $(n + 1)$ th, we immediately get a_n^+ = 0 for odd *n*, as indeed it must for a

symmetric free energy. By the same argument which led to Eq. (45), we have

$$
\alpha_0^{\;\;+} - \alpha_2^{\;\;+} - \alpha_{n-2}^{\;\;+} + \alpha_n^{\;\;+} \leq 0; \; n = 4, \; 6, \; \ldots \qquad (46)
$$

For the β 's, since all the $\Pi_n(F,H)$'s may be present, we have

$$
\beta_0 - \beta_1 - \beta_{n-1} + \beta_n \le 0; \ n = 2, 3, \dots \tag{47}
$$

from the above arguments applied to Eqs. (33a), (33b) and (33c). Equations (45), (46), and (47) constitute all the unmixed relations among critical exponents for a magnetic system. (We use the word "unmixed" to denote the fact that each relation involves only exponents of the same type.) The analysis of mixed relations of the type given by Eqs. (36c) and (36d) is more complicated, except when $P(F; H, t)$ is homogeneous, and will not be done here.

In the case of fluids, one has the choice of using the grand potential per unit volume (p) whose natural variables are the chemical potential and the temperature, or the Gibbs function per mole (chemical potential) whose natural variables are the pressure and the temperature. For the purpose of comparison with experimental results, it is preferable to use the latter since the pressure is the natural variable for measurement. However, before the above analysis can be applied, a transformation to the variable which describes the coexistence curve must be effected. Thus, the function to be examined can be written as $\mu = \mu(\pi, t)$, where $\pi = p - p_{\pi}(t)$, with $p_{\pi}(t)$ the vapor pressurfor $t < 0$. Because of the complications which this singular transformation introduces (for example, difficulty in treating isobars which
are currently in vogue experimentally),²¹ we are currently in vogue experimentally),²¹ we shall reserve the analysis for the future.

IV. EXAMPLES OF ALGEBRAIC FUNCTIONS

We have already presented the algebraic function which coincides with the Weiss (molec ular) field theory in the neighborhood of the critical point. In this section, we give some examples of homogeneous algebraic functions which have the same sets of critical exponents presented by Griffiths' in a recent paper as well as one example of an inhomogeneous algepresented by Crimius- in a recent paper as
well as one example of an inhomogeneous algebraic function.²² Inhomogeneous functions are more useful, as there is experimental evidence that the primed and unprimed exponents are not equal, 23 and (for a fluid) that the liquid and vapor exponents are also unequal. 24

Example 1.
$$
\beta = \frac{1}{8}
$$
, $\delta = 15$, $\gamma' = \frac{7}{4}$, $\alpha' = 0$.

These are the recognized indices for the twodimensional Ising model. Since we are using functions which are algebraic in both H and $t, \alpha' = 0$ denotes a discontinuity in the specific heat rather than a logarithmic singularity. We shall make no attempt to fit the critical point

coefficients but, rather, write down the simplest polynomial which leads to the indicated critical exponents. This is given by

$$
P(F; H, t) = F7(F + t2)8 + H16
$$

+ 2tH⁸F⁷ + t¹⁵H⁸ = 0. (48)

The last two terms are needed to assure the convexity conditions on F . Note that the coefficient $b_-(t)$ which determines β is found from the eighth recursion relation [Eq. (25)] rather than the second, as the first seven are identically zero.

Example 2.
$$
\beta = \frac{1}{3}, \delta = 5, \gamma' = \frac{4}{3}, \alpha' = 0.
$$

These indices are close to those found for a number of fluids and ferromagnets. The simplest defining polynomial is

$$
P(F; H, t) = F4(F + t2)6 + H12
$$

-2t²H⁶F⁴ + t¹⁰H⁶ = 0. (49)

Since $1/\beta$ is an odd integer and F is symmetrical in H , we find that F is also symmetrical in t . Hence, there will be a spontaneous magnetization for $t>0$ as well as for $t<0$, but, if we start on the branch of F which has a spontaneous magnetization for $t<0$, then analytic continuation along the real H and t axes will lead us to the branch of F which has zero magnetization at zero applied field for $t > 0$. However, if we stick to the minimum principle, then this example shows that it is impossible to construct a homogeneous algebraic function with the given exponents, and which satisfies the minimum principle wherever it yields a physical free energy.

Example 3.
$$
\beta = \frac{5}{16}, \delta = 5, \gamma' = \frac{5}{4}, \alpha' = \frac{1}{8}.
$$

This set of critical exponents and those of the next example are close to the estimates for the three-dimensional Ising model based on series expansions. The present case is simple because $1/\beta$ has an even numerator and δ is an odd integer. The defining polynomial is therefore

 $\mathbf{F}_{\mathbf{r}}$ = $\mathbf{F}_{\mathbf{r}}$ to $\mathbf{F}_{\mathbf{r}}$ the integration of $\mathbf{F}_{\mathbf{r}}$

$$
P(F; H, t) = F^{4}(F^{8} + t^{15})^{2} + H^{24}
$$

+ 2t¹⁰H²F¹³ + t²⁵H²F⁵ = 0. (50)
Example 4. $\beta = \frac{5}{16}$, $\delta = \frac{26}{5}$, $\gamma' = \frac{21}{16}$, $\alpha' = \frac{1}{16}$.

The fact that δ is not an odd integer, or even that it does not have an odd numerator, poses no difficulty. The defining polynomial is

$$
P(F; H, t) = F^{20}(F^{16} + t^{31})^2 - H^{62}
$$

+ 3t⁵¹H²F²⁴ + 2t⁸²H²F⁸ = 0. (51)

Equation (51) illustrates the form of Eq. (12b) since $P(F; H, 0) = (F^{26} + H^{31})(F^{26} - H^{31})$. Note that in these first four examples, the coefficient $c_{\perp}(t) = 0$, so that γ is undefined.

Example 5.
$$
\alpha = \frac{1}{5}
$$
, $\alpha' = \frac{1}{8}$; $\beta = \frac{1}{4}$, $\gamma = \frac{8}{5}$, $\gamma' = \frac{11}{8}$;
\n $\delta = 7$; $\epsilon = \frac{4}{7}$; $\phi = \frac{2}{7}$.

This set of critical exponents does not correspond to any known system but was chosen to illustrate how inhomogeneous algebraic functions can easily generate unequal primed and unprimed critical exponents. The defining polynomial is

$$
P(F; H, t) = (F^8 + t^{15})^2 (F^5 + t^9) + H^{24}
$$

+ $t^2 H^2 F^{18} + t H^{20} F^2 = 0.$ (52)

Solution of the recursion relations, Eqs. (25) and (26), yields the following for the coefficients ^a to f:

$$
a_{-} = -(-t)^{\frac{15}{8}}, \qquad a_{+} = -t^{\frac{9}{8}};
$$
 (53a)

$$
b_{-} = \pm \frac{1}{8} (-t)^{\frac{1}{4}}, \qquad b_{+} = 0; \tag{53b}
$$

$$
c_{-} = -\frac{1}{32}(-t)^{-\frac{11}{8}}, \quad c_{+} = -\frac{1}{5}t^{-\frac{8}{5}};
$$
 (53c)

$$
d = -H^{\frac{8}{7}};
$$
 (53d)

$$
e = \frac{1}{21}H^{\frac{4}{7}}; \tag{53e}
$$

$$
f = -\frac{1}{21}H^{-\frac{2}{7}}.
$$
 (53f)

The critical exponents obtained from these coefficients satisfy the following equations:

$$
\alpha' + 2\beta + \gamma' = 2 \tag{54a}
$$

$$
\alpha + 2\beta + \gamma = 2 \tag{54a}
$$

2\epsilon + \phi - 1/\delta = \frac{9}{7} > 1 \tag{54b}

$$
\alpha' + \beta(\delta + 1) = \frac{17}{8} > 2
$$
 (54c)

$$
\epsilon (2-\alpha')/(1-\alpha')-1/\delta = \frac{53}{49} > 1. \tag{54d}
$$

V. CONCLUSION

The foregoing analysis provides the following picture of a phase transition with a critical point. First, the critical point itself is a branch point in the naturally intensive variables of the appropriate thermodynamic potential. Second, the coexistence curve is (at least) a line of crunodes. Third, by the theorem of continuity, this line of singularities is extended above $T = T_{c}$, but disappears from what we may loosely refer to as the physical sheet and appears on a non-physical branch of the thermodynamic potential. This is illustrated specifically by the presence of a line of acnodes in the classical theory as exemplified by the weiss field theory of ferromagnetism. Thus,
the idea of Douglass,²⁵ that the two phases of the idea of Douglass,²⁵ that the two phases of a system may be distinguishable above the critical point, is partially vindicated, but the distinction exists on a non-physical portion of the function representing the appropriate free energy. Finally, we have seen that for algebraic functions at least, the thermodynamic potential, although analytically continuable in both variables from liquid to vapor, splits into two separate functions of the temperature on the coexistence curve

 $(H = 0$ for a magnetic system). This behavior is illustrated even in the classical theory. The thermodynamic potential may split into two separate functions of the applied field or the pressure on the critical isotherm. This provides an explanation for the fact that the critical exponent 5 need not necessarily have an odd numerator.

As the title of this paper implieg, we have demonstrated the need and usefulness of the theory of functions of several complex variables in the treatment of equilibrium critical phenomena. Actually, the subject has just barely begun since we have restricted the analysis here to a particular class of functions, namely those which are algebraic in the thermodynamic variables. Whatever is the nature of the true thermodynamic potentials, these functions may be thought of as being asymptotically equivalent to them and, in the region in which they fit the experimental information, the relations derived above among their critical exponents must hold. It might be interesting, however, to speculate on the effect which the introduction of other singularities might have on the behavior of various thermodynamic functions in the neighborhood of a singular point of the free energy. An hood of a singular point of the free energy.
example of this is the proposal by Fisher,²⁶ based on an extension of the droplet model.²⁷ $\frac{1}{27}$ that the coexistence curve may consist of a line of essential singularities, although, by the theorem of continuity of singularities in several complex variables, there must then be essential singularities elsewhere. Another problem is the apparent lack of what we may call symmetrydestroying terms in the defining polynomial for the algebraic function representing a fluid. Experimentally, one finds that the thermodynamic inequalities corresponding to Eqs. (25) are satisfied with the equality sign to within the limits of experimental error. Thus, there are a number of directions in which one can proceed. One is to try to use algebraic functions in the analysis of other singular thermodynamic points such as the triple point and the λ point. Another is to generalize the concept of algebraic function to include functions with irrational critical exponents as well as other types of singularities. Finally, there is the problem mentioned earlier of justifying the use of analytic thermodynamic functions by means of statistical mechanics applied to certain classes of realistic Hamiltonians. In the final analysis, however, it is really nature which can justify this concept, so that the main burden is to deduce as much as possible to compare with known results, be they actual experiments or solutions of statistical mechanical models.

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 ${}^6G.$ S. Rushbrooke, J. Chem. Phys. 39, 842 (1963). 7 See, for example, R. C. Gunning and H. Rossi,

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⁹See C. Kittel, Solid State Physics (John Wiley & Sons, Inc. , New York 1956), Chap. 15.

 10 Rudolph C. Hwa and V. L. Teplitz, Homology and Feynman Integrals (W. A. Benjamin, Inc. , New York, 1966).

 $¹¹$ This accident has already been noted by Widom (Ref.</sup> 5) in a different form since his homogeneous functions are generalizations of the simplest one, which is the classical equation of state.

An example pertaining to analysis of experimental data is given by M. H. Coopersmith, Phys. Rev. . Letters 20, 432 (1968).

13See, for example, L. V. Ahlfors, Complex Analysis (McGraw-Hill Book Company, Inc., New York, 1953), p. 227.

 14 L. P. Kadanoff, Physics 2, 263 (1966). See also B. Widom, Ref. 5 and C. Domb and D. L. Hunter, Ref. 18.

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 17 J. W. Essam and M. E. Fisher, J. Chem. Phys. 38, 802 (1963).

 78 J. S. Kouvel and D. S. Rodbell, Phys. Rev. Letters 18, 215 (1967). Note that $\alpha_4 = \kappa - 4\gamma$.

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 22 This example is similar to the one given in Ref. 16, but is elaborated on here.

 23 See, for example, M. R. Moldover, and W. Little in Critical Phenomena, edited by M. S. Green and J. V. Sengers (National Bureau of Standards Report No. 273, 1966).

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²⁷See J. Frenkel, Kinetic Theory of Liquids (Oxford University Press, London, 1946), Chap. 7.

Announcement: Comments and Addenda

^A new section, "Comments and Addenda, " has been established in The Physical Review, to meet a long-standing need for a place to publish short communications which are not of such urgency as to justify publication in Physical Review Letters and are not appropriate for regular Articles. ' This section includes only the following types of communications:

1. Comments on papers previously published in The Physical Review or Physical Review Letters. Comments by others than the authors of the work being discussed will normally be sent to the latter to solicit their opinion, and to give them the opportunity (if the situation warrants it) of submitting a comment in reply for simultaneous publication.

2. Addenda to papers previously published in The Physical Review or Physical Review Letters, in which the additional information can be presented without the need for writing a complete article.

It should be noted that this new section is not intended as a medium for polemics, nor as a haven for poorly written short communications which would be more understandable and useful if written up in the normal format of a short article.

Manuscripts intended for this section may be accompanied by a brief abstract for information retrieval purposes. Accepted manuscripts will follow the same publication schedule as articles in this journal, and galleys will be sent to authors.