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CRITICAL POINT PHENOMENA — THE ROLE OF SERIES EXPANSIONS

MICHAEL E. FISHER

ABSTRACT. The use of series expansions to determine the nature of critical point singularities, especially the values of the critical exponents, is reviewed. Ratio techniques, based on extrapolation of the ratios of successive expansion coefficients, and Padé approximant methods, utilizing logarithmic derivatives, are explained, illustrated, and compared.

1. **Introduction.** In this lecture I will survey briefly the phenomena observed near the critical point of a system. The range of behavior is very varied and we shall only examine one or two typical examples. The main aim will be to establish the existence of the so-called "critical point exponents" which describe the nature of the mathematical singularities exhibited by the different thermodynamic functions as the critical point is approached. The theory of these singularities may be developed via suitable statistical-mechanical models which, while caricatures of a realistic physical system, retain such vital features as the dimensionality of space, the finite range of the interactions, and certain basic symmetry properties.

These models in turn are usually intractable as regards exact mathematical analysis. However, general methods can be developed which yield power series expansions for many functions of interest; frequently between 8 to 30 leading coefficients of such power series can be obtained. The problem is then a numerical one of extrapolating the series in such a way as to estimate the nature of the particular critical point singularity and the behavior of the function in its vicinity. I will show how this can, in favorable cases, be handled by studying the ratios of successive expansion coefficients. The method was pioneered by Domb and his coworkers, especially Sykes and Fisher [1], [2]. The reliability of the techniques can be tested against the relatively few closed form mathematical results, in particular, Onsager's renowned solution of the two-dimensional Ising models [3].

In less favorable examples this approach fails, and then, as first demonstrated by Baker [3], Padé approximants have a vital role to play. In a number of important cases the intelligent application of Padé approximants has been strikingly successful [3], [4]. Such techniques have thus established a central place for themselves in the

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study of critical phenomena and, more generally, in the statistical mechanics of many-particle systems.

In this lecture I shall be able to present only a rather rapid survey. More detailed reviews have been given by the author [6], [7], and, more recently, by Gaunt and Guttman [8] and by Hunter and Baker [9].

2. **Critical Phenomena.** If a gas is compressed at a high enough temperature its density ρ increases continuously and monotonically with pressure p, until it is a dense fluid indistinguishable from a normal liquid. On the other hand if the same gas is compressed at a temperature below its critical temperature $T = T_c$, the density ρ exhibits a jump discontinuity from a relatively low gas (or vapor) density $\rho_G(T)$ to a much higher liquid density $\rho_L(T)$. Since, at these two densities, both liquid and vapor can coexist in equilibrium in the same container, the function

$$\Delta\rho(T) = \rho_L(T) - \rho_G(T), \tag{2.1}$$

is referred to as the "coexistence curve." As T is raised towards T_c it is found that $\Delta\rho$ decreases monotonically, finally vanishing identically at T_c where $\rho_L(T) = \rho_G(T) = \rho_c$. Some data for carbon dioxide [10] are displayed in Figure 1: note that the temperatures go to within a millidegree of T_c ($=304°$ K) but that the scale, with

$$\Delta T = |T - T_c|, \tag{2.2}$$

is nonlinear, the ordinate being proportional to $\Delta T^{1/3}$. The observations may be summarized accurately by

$$\Delta\rho/\rho_c \approx A(\Delta T/T_c)^\beta, \tag{2.3}$$

where A is a constant amplitude, while the "critical exponent" β is evidently very close to 1/3; in fact the relation (2.3) holds over three or four decades in $\Delta T/T_c$, and corrections become significant only for $\Delta T/T_c \geqq 0.01$. Furthermore the "one third" value for the exponent β seems to be "universal", applying within experimental precision to all gases and, indeed, even to fluid mixtures. Thus accurate measurements for xenon indicate $\beta = 0.343 \pm 0.005$.

More surprising still is the fact that if one studies ferromagnets one obtains closely analogous results. If $M(H, T)$ is the magnetization as a function of magnetic field H, and temperature T, one discovers a discontinuity of magnitude

$$\Delta M = 2M_0(T) = \lim_{H\to 0+} [M(H, T) - M(-H, T)], \tag{2.4}$$

as a function of the field. The spontaneous magnetization $M_0(T)$, so defined, vanishes abruptly at the Curie temperature T_c (which is nothing but a magnetic critical temperature) according to the law

$$M_0(T) \approx A(\Delta T/T_c)^{\beta}, \qquad (T \to T_c-). \tag{2.5}$$

Despite many approximate theories which predict $\beta = 1/2$ (see e.g. the reviews [6], [7]), one observes experimentally that β lies in the range 0.33 to 0.35, just as for fluids!

Different physical variables and different directions of approach to a critical point, yield different exponents, although their values are apparently still "universal" over a given class of systems. Thus, for the compressibility of a fluid on approach to the critical temperature from above, one has

$$K_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial p}\right)_T \sim \left(\frac{\Delta T}{T_c}\right)^{-\gamma} \to \infty, \qquad (\rho = \rho_c, T \to T_c+). \tag{2.6}$$

This defines the important exponent γ. Similarly for the susceptibility of a ferromagnet one has

$$\chi_T = \left(\frac{\partial M}{\partial H}\right)_T \sim \left(\frac{\Delta T}{T_c}\right)^{-\gamma} \to \infty, \qquad (H = 0, T \to T_c+). \tag{2.7}$$

For fluids one finds $\gamma \simeq 1.22$ to 1.25; in this case ferromagnets seem to be characterized by a higher value, namely, $\gamma \simeq 1.33$ to 1.38. This difference is now believed to be associated with the presence of a continuous rotational symmetry for typical ferromagnets. Further aspects of the theory of critical phenomena are reviewed in References [6], [7], and [11].

3. **Formal Exponent Definitions.** For mathematical work one needs a more precise definition of a critical exponent. Since the power law behavior is expected to hold only asymptotically as the critical point is approached, we write

$$f(x) \sim x^{\lambda} \quad \text{as} \quad x \to 0+, \tag{3.1}$$

to mean

$$\lim_{x \to 0+} [\ln f(x)/\ln x] = \lambda. \tag{3.2}$$

In principle, of course, this limit might not exist; in such a case it would normally be appropriate to replace lim by lim sup. From both numerical and analytical viewpoints it is useful, however, to distinguish more detailed cases as follows:

(3.3) (a) Pure power law $f(x) = Ax^{\lambda}$;

(3.4) (b) Simple singularity $f(x) = x^{\lambda}f_0(x)$,

with $f_0(x)$ analytic in the neighborhood of $x = 0$;

(c) Complex singularities

(i) coincident weaker singularities, such as

$$f_0(x) = f_0 + f_1x^{\lambda_1} \; (0 < \lambda_1 < 1), \tag{3.5}$$

(ii) coincident divergent singularities, such as

$$f_0 = (\ln x^{-1})^{\lambda_1}f_{00}(x), \tag{3.6}$$

with $\lambda_1 \neq 0$ and, say, $f_{00}(x)$ analytic near $x = 0$.

The presence of logarithmic factors, as in this last case, is by no means purely academic. Figure 2 displays remarkable data obtained recently by Ahlers [12] for the specific heat, $C(T)$, of liquid helium at the so-called lambda transition, below which helium becomes a superfluid. In this case the transition point T_λ ($\equiv T_c$) is determined to one part in 10^{-7}, and the data are linear versus $\log(\Delta T/T_c)$ over four decades of temperature! (The two curves in Figure 2 represent data above and below T_λ, respectively.) To high precision one finds

$$C(T) \approx A_\pm \ln(\Delta T/T_c)^{-1} + B_\pm, \; (T \to T_c \pm), \tag{3.7}$$

with $B_+ < B_-$ and $A_+ \simeq A_-$. More generally, to describe specific heat singularities, one writes

$$C(T) \sim (\Delta T/T_c)^{-\alpha}. \tag{3.8}$$

Simple logarithmic behavior of the form (3.7), is then accommodated by differentiating sufficiently often until a power law divergence is obtained; on writing

$$\frac{d^kf}{dx^k} \sim x^{-k+\lambda_s} \to \infty, x \to 0+, \tag{3.9}$$

the corresponding 'singular-part' exponent, λ_s, is defined in a natural way. The data on helium at the lambda point are thus described by $\alpha_s = 0$ (and $k = 1$ suffices); for many ferromagnets one finds $\alpha_s \simeq -0.1$, corresponding to a finite but cuspoidal singularity in $C(T)$ [7].

4. **The Ising Model.** At this point in time the theorist studying critical phenomena has quite a battery of different statistical mechanical models in his repertoire. Undoubtedly the most important, the best understood, and the most widely applied model is the Ising model (see [3], [6], [7]). A brief description of this model will serve to give

an impression of the general picture. The Ising model is most easily thought of as describing a highly anisotropic magnetic system in which each "spin" or "microscopic magnet," s_i, associated with a crystal lattice site i, can point only "up" or "down." More formally let $i = 1, 2, \cdots N$ label the sites of a regular d-dimensional space lattice (e.g., a simple hypercubic lattice with coordinates vectors $r_i = (n_i^{(1)}a, n_i^{(2)}a, \cdots, n_i^{(d)}a)$ where the $n_i^{(k)}$ are integers and a is the lattice spacing). Associated with each site i is a spin variable, which takes the values $s_i = +1$ or -1, only. Each spin configuration $\{s_i\}$ of the whole lattice has an energy which (in the simplest case) is taken to be

$$E\{s_i\} = -J \sum_{(ij)} s_i s_j - H \sum_{i=1}^{N} s_i. \tag{4.1}$$

Here the first sum runs over nearest neighbor pairs in the lattice; for $J > 0$ this term associates a lower, favorable energy with a pair of adjacent spins "pointing the same way" (i.e., $s_i = s_j = +1$ or $s_i = s_j = -1$). The term proportional to the field, H, favors alignment of the spins with the same sense as H. (Note that the model may be interpreted as a 'lattice gas' of nonoverlapping particles, by identifying $s_i = +1$ as an empty site, while letting $s_i = -1$ denote the presence of a particle at site i.)

Following Gibbs' basic statistical postulate one now defines the partition function

$$Z_N(H, T) = \sum_{\{s_i = \pm 1\}} \exp\{E\{s_i\}/k_B T\} = \sum_{\{s_i\}} e^{K\Sigma s_i s_j + L\Sigma s_i}, \tag{4.2}$$

where T is the temperature, k_B is Boltzmann's constant, while the basic dimensionless variables are

$$K = J/k_B T \quad \text{and} \quad L = H/k_B T. \tag{4.3}$$

All the observable thermodynamic properties, such as the magnetization, specific heat, etc., now follow by taking derivatives of the fundamental thermodynamic potential, or "free energy," namely

$$f(H, T) = \lim_{N \to \infty} N^{-1} \ln Z_N(H, T). \tag{4.4}$$

The limit operation involved here is essential for any serious discussion of critical phenomena, since no true mathematical singularities are present for finite N. Clearly, however, this 'thermodynamic limit' accounts for much of the mathematical difficulty of the problem.

In the famous work already alluded to, Onsager [3] calculated analytically the partition function, $Z_N(0, T)$, and the free energy

$f(0, T)$ in zero field ($H = 0$) for the two-dimensional ($d = 2$) Ising model. He obtained the specific heat in terms of elliptic integrals; from this result the exponent is found to be $\alpha_s = 0$, corresponding to the expression (3.7) (with, in fact $A_+ = A_-$ and $B_+ = B_-$). He also showed (see [6], [7]) that the spontaneous magnetization of the square lattice is

$$M_0(T) = [1 - (\sinh 2K)^{-4}]^{1/8}, \qquad (T \leqq T_c). \tag{4.5}$$

On comparison with (2.5) we find $\beta = 1/8$. Further analytical work (see [7]) shows that the susceptibility exponent is $\gamma = 1\frac{3}{4}$.

Unfortunately no comparable closed formulae have been obtained for dimensions $d > 2$, nor even for nonzero field when $d = 2$; the problem is one of "classic difficulty"! (The case $d = 1$ is trivial but no proper critical point exists.) Rigorous mathematical results concerning the existence of a phase transition, the analyticity of $f(H, T)$ for $H \neq 0$, and bounds on T_c, have been found. Such results, however, say nothing about the values of the critical exponents; all that has been proved in that direction are inequalities such as

$$\alpha' + 2\beta + \gamma' \geqq 2, \tag{4.6}$$

where the primes denote the approach of T to T_c from below (see [6] and [7]). While this, and some similar inequalities appear, in fact, to be best possible (i.e., to hold on equalities, [6], [7], [11]) they clearly leave much to be desired.

5. **Series Expansions.** In the face of the profound analytical difficulties, progress has been made by generating power series expansions for the properties of interest. Some of the most informative expansions follow by introducing the identity

$$e^{Ks_i s_j} = (\cosh K)[1 + v s_i s_j], \tag{5.1}$$

$$v = \tanh K = \tanh(J/k_B T), \tag{5.2}$$

which holds since $s_i s_j = \pm 1$. Substitution in (4.2), and formal expansion in powers of v, leads to expansions of the free energy $f(H, T)$ and its derivatives, in which the coefficients can be expressed in "diagrammatic" or "graphical" terms [6], [7]. For example, the zero field susceptibility above T_c has the expansion

$$\chi(T) = \sum_{n=0} a_n v^n, \tag{5.3}$$

where the coefficients are given by

$$a_n = \sum_G w(G_l^n)\pi(G_l^n; \mathcal{L}). \tag{5.4}$$

Here the sum runs over all linear graphs, G_l^n, of l points (or vertices) and n lines (or edges); $w(G)$ is a weight factor depending only on the graph G; the 'lattice constant' $\pi(G; \mathcal{L})$ counts the number of ways the graph G can be *embedded* in the particular lattice $\mathcal{L}$ (now conceived as an infinite graph with its lines connecting nearest neighbor sites or points). The leading coefficients a_n for the square ($d = 2$), and simple cubic ($d = 3$) lattices, are shown in Table I. (At present the square lattice series is known up to a_{21}, [12].) For the susceptibility, the dominant graphical contribution comes from the number, c_n, of n-step self-avoiding walks (linear chains) which can be drawn on the lattice starting at the origin. These numbers are shown in Table I for comparison.

As can easily be imagined from the size of the integers involved, these data are not easy to obtain. (The last known coefficient for the body centered cubic lattice is $a_{15} = 2\,665\,987\,056\,200$, [**12**].) Indeed, special methods have been developed, especially by Sykes, and his collaborators (see [**6**], [7], [13], [14]), in order to calculate them (correctly!). Electronic computers are a help, but they have a poor geometrical and topological sense, and by no means deliver an easy salvation. In the case of less intensively studied functions and models, often only 9 to 12 exact coefficients are available.

Other expansions can be obtained which are valid at high fields, in terms of the variable $y = e^{-2L} = \exp(-2H/k_BT)$, and at low temperatures, in terms of $x = e^{-2K} = \exp(-2J/k_BT)$. Formulae analogous to (5.4) hold, but the definitions of the weight factors are more complicated. However, in all cases the uniformity of the underlying lattice, and the increasing number of graphs contributing in higher orders, encourages the hope that the expansion coefficients should, in turn, display some sort of regularity.

6. **Ratio Analysis of Series Expansions.** In order to draw useful conclusions concerning critical point singularities from a truncated series such as (5.3), it is clearly pointless merely to sum the first N available terms; some method of extrapolation is essential. Now the positive and monotonically increasing nature of the known coefficients a_n displayed in Table I, suggests that $\chi(v)$ belongs to the class (A) of functions

$$F(z) = \sum_{n=0} a_n z^n, \tag{6.1}$$

with non-negative Taylor series coefficients a_n. (One might hope to prove this in certain cases but it does not seem at all easy.) For such a function, the nearest singularities to the origin of the complex z-plane include the "physical singularity" on the real positive axis at

$$z = z_c = \lim_{n \to \infty} |a_n|^{-1/n}, \tag{6.2}$$

This singularity will normally be the dominant, i.e., strongest, singularity.

One might try to estimate z_c by extrapolating the nth roots of the coefficients a_n, but, by considering simple examples, it is easy to see that this will usually yield a very slowly convergent sequence which is hard to extrapolate reliably. A much better procedure [1], [2] is to study the successive ratios

$$\mu_n = a_n/a_{n-1}, \tag{6.3}$$

for which one has

$$\lim_{n \to \infty} \mu_n = \mu = 1/z_c, \tag{6.4}$$

whenever the limit exists. A plot versus $1/n$ of the ratios μ_n (normalized by the lattice coordination number q) is shown in Figure 3, for the susceptibility of triangular ($d = 2$), and face centered cubic ($d = 3$) Ising lattices; a striking linearity is observed. (The reader is urged to construct similar plots with the data of Table I; on doing so one discovers the same linear behavior but with a superimposed odd-even oscillation.) The observed linearity suggests construction of the linear extrapolants

$$\mu_n' = (n + \epsilon)\mu_n - (n + \epsilon - 1)\mu_{n-1}, \tag{6.5}$$

or, for a sequence of ratios with an oscillatory component,

$$\mu_n'' = \tfrac{1}{2}[(n + \epsilon)\mu_n - (n + \epsilon - 2)\mu_{n-2}]. \tag{6.6}$$

Here ϵ is a small number (the n-shift) which may be varied to obtain a number of sequences converging to the limit μ_∞ at different rates and from different directions. The triangular lattice data, to $n = 12$, yield the sequences $\mu_n'' = \cdots 3.7395, 3.7381, 3.7369$, for $\epsilon = 0$, and $\mu_n'' \simeq \cdots 3.7228, 3.7245, 3.7257$, for $\epsilon = \frac{1}{2}$; these indicate a limit $\mu = 3.731 \pm 0.002$. This, in turn, may be compared with the *exact* result $\mu_\infty = 2 + \sqrt{3} = 3.7320\cdots$ due to Onsager (see [7]). The agreement is very encouraging and is confirmed more closely by further terms in the expansion. By this same method and various refinements, the critical points of all the usual three-dimensional lattices have been estimated to an apparent precision of 1 part in 10^4 or better. Of course one does not have rigorous error bounds in such work; but the comparison with the closely analogous but exactly soluble cases, provides strong presumptive evidence.

Of greater significance than the position, z_c, of the singularity is the value of the corresponding critical exponent. If the linear behavior of the ratios is truly asymptotic, so that,

$$\mu_n = \mu[1 + (g/n) + o(1/n)], \tag{6.7}$$

where g is the limiting slope of the $1/n$ plot, we have

$$a_n \approx A\binom{g+n}{n}\mu^n = A\binom{-1-g}{n}(-\mu)^n \approx \frac{An^g\mu^n}{\Gamma(1+g)}. \tag{6.8}$$

It then follows from Appell's comparison theorem that (for $g > -1$)

$$F(z) = \frac{A}{(1-\mu z)^{1+g}}\{1 + o(z - z_c)\}, \qquad (z \to z_c-). \tag{6.9}$$

Thus if the function under study is the susceptibility χ, the corresponding critical exponent is given simply by

$$\gamma = 1 + g. \tag{6.10}$$

The limiting slope, g, may be estimated from sequences such as

$$g_n = (n+\epsilon)[(\mu_n/\tilde{\mu}) - 1] \qquad \text{and} \qquad \overline{g_n} = \tfrac{1}{2}(g_n + g_{n-1}), \tag{6.11}$$

where $\tilde{\mu}$ is the exact limit μ, if known, or, otherwise the best available estimate. (An interesting example in which μ $(=1)$ is known, is provided by the coefficients $a_n = \langle R_n^2 \rangle$, representing the mean square end-to-end distance of all n-step self-avoiding walks [17].)

This method can again be tested on the two-dimensional Ising model; it is found to work very well. For the simple cubic ($d = 3$) lattice the critical point estimate $\mu = 1/v_c \simeq 4.5840$ yields the sequence $\overline{g_n} = \cdots$, 0.248, 0.2506, 0.2488, 0.2505, 0.2495 up to $n = 11$. (The reader may carry this further with the data of Table I). The results suggest $g = 0.250 \pm 0.001$ or, allowing for the (apparent) uncertainty in μ, $g = 0.250 \pm 0.005$. The behavior of estimates for the body-centered, face-centered and diamond lattices is equally regular and numerically almost identical [1], [13]. One is led strongly to conjecture that the exact exponent for all the three-dimensional lattices is $\gamma = 1.250 = 1\frac{1}{4}$! This contrasts with the known two-dimensional result, $\gamma = 1\frac{3}{4}$. The validity of the estimate $\gamma \simeq 1.25$ has been confirmed strikingly by experiments on the binary alloy beta-brass (approximately 50 : 50 Cu : Zn for which the Ising model is a fairly accurate representation of reality [15]. Other alloys such as Fe_3Al yield similar results.

These ratio extrapolation methods may be developed considerably. If the value of the exponent $1 + g$ is known (or strongly suspected) improved estimates of the critical point can usually be found from the sequence

$$\mu_n{}^* = \mu_n(n + \epsilon)/(n + \epsilon + g), \tag{6.12}$$

which should approach μ more rapidly than $1/n$. The amplitude A of the singularity in (6.9) can be estimated by matching the known coefficients to the form (6.8). Given the first N coefficients a_n, and reliable estimates $\tilde{g}$, $\tilde{\mu}$, and $\tilde{A}$, of g, μ, and A, the behavior of the function $F(z)$ may be approximated for $|z| < z_c$ by

$$F(z) \simeq \sum_{n=0}^{N} a_n z^n + R_N(z) \tag{6.13}$$

where

$$R_N(z) = \tilde{A} \left[(1 - \tilde{\mu}z)^{-1-\tilde{g}} - \sum_{n=0}^{N} \binom{n + \tilde{g}}{n} \tilde{\mu}^n \right]. \tag{6.14}$$

Other refinements of the technique can be used to study weaker singularities, such as often occur at $z = -|z_c|$, by dividing out the dominant singularity and studying the ratios of the resulting coefficients (see [6], [7]). Given long enough series, it is even possible to estimate the nature of coincident singularities of the type indicated in (3.5). On the other hand, as one may show by constructing examples like (3.5) and (3.6), the methods can fail to reveal the true nature of a singularity if there is a strong close-by or coincident singularity [e.g., a small value of λ_1 in (3.5)], or if there are logarithmic factors, as in (3.6). Even in such cases, however, the numerical values of the function will normally be quite well represented by approximants such as (6.13), even close to the singularity.

Finally, it is worth noting that the ratio techniques are invariant to transformations of the type

$$F(z) \Rightarrow \tilde{F}(z) = hz^j F(z) + k(z), \tag{6.15}$$

where h is a constant, j is a small integer (say $\geqq 5$) and $k(z)$ is a low order polynomial (of degree, say, $\leqq 5$). Although this remark is not at all profound it is quite significant in practice since one does not have to worry about questions of "normalization" or additive "backgrounds."

Furthermore this invariance property is *not* shared by the Padé approximant techniques to be described next.

7. **Padé Approximant Analysis.** Unfortunately not all functions of practical interest belong to class (A), that is, have positive expansion coefficients. Consider, in particular, the series exhibited in Table II, for the spontaneous magnetization $M_0(T)$ of the face centered cubic Ising lattice, which one would like to analyze to determine the exponent β [defined in (2.3) and (2.5)]. The magnitudes of the terms are quite irregular and the sequence of signs seems random! Clearly no information can be gained by the ratio technique. The mathematical implication of such a class (B) expansion, is merely that the dominant singularity (or conjugate pair of singularities) lying closest to the origin of the z-plane is no longer the physical singularity (which is always the nearest singularity on the real positive axis).

What is thus required is an effective (numerical) method of analytical continuation, which will serve to carry the function beyond the circle of convergence determined by the closest, but nonphysical singularities. For such a task, Padé approximants are ideally suited. However, there is comparatively little to be gained by forming direct Padé approximants to a series such as that in Table II. The reason is simply that while Padé approximants will provide rapid convergence to a function in the vicinity of a simple zero or pole, they cannot converge well near a branch point of the form $(z_c - z)^\beta$, such as is expected in functions like M_0. (Numerical experiments reveal that Padé approximants represent the branch cuts, necessitated by their single valuedness, by an interlacing sequence of zeros and poles [15]; convergence near such a cut is consequently slow and irregular.) A successful route past this obstacle was first demonstrated by Baker [4]: suppose we can write

$$F(z) = \sum_{n=0}^{\infty} a_n z^n = (1 - \mu z)^\beta C(z), \tag{7.1}$$

where $C(z)$ is analytic and nonzero in the vicinity of $z = z_c = 1/\mu$ or, at least, is only weakly singular there [for example like (3.5) with $\lambda_1 > 1$]. Then consider the logarithmic derivative

$$D(z) = \frac{d}{dz}\ln F(z) = \sum_{n=0}^{\infty} d_n z^n = \frac{\beta}{z - z_c} + \frac{d}{dz}\ln C(z). \tag{7.2}$$

Evidently the branch point has become merely a simple pole. Consequently we may hope that Padé approximants, defined, as usual, by

$$[L/M]_{D(z)} = \frac{P_L(z)}{Q_M(z)} = \frac{p_0 + p_1 z + \cdots + p_L z^L}{1 + q_1 z + \cdots + q_M z^M}, \tag{7.3}$$
$$= \sum_{n=0}^{L+M} d_n z^n + O(z^{L+M+1}),$$

will converge well even in the immediate neighborhood of the singularity z_c. In practice, given the coefficients a_n for $n \leqq N$, one calculates the coefficients d_n (by a straightforward recursion relation), computes the approximants $[L/M]_D$ for $L + M \leqq N$, and then studies their poles in the vicinity of the expected critical point. The locations of these poles provide estimates for z_c; but, more importantly, by (7.2), the residues at the poles represent estimates for the exponent β. In view of the well known invariance of the diagonal approximants $[M/M]$, under Euler transformations, [4], [**16**], attention is mainly focussed on the diagonal, and near-diagonal, $[M/(M + J)]$, sequences.

Of course, this method of analysis is not confined to functions of class (B). It may, indeed, be tested on the class (A) high temperature Ising model susceptibility expansions. Table III displays the poles and residues of the first few diagonal approximants calculated from the data of Table I. The agreement of the estimates with the exact results (for the $d = 2$, square lattice), and with the previous ratio estimates (for the $d = 3$, simple cubic lattice), is most impressive! Furthermore the concordance improves rapidly as further terms are added, the latest estimate for the simple cubic critical point being $v_c = 0.21813 \pm 1$ [13].

If the critical point z_c is already known, refined estimates of the critical exponent may be obtained by defining the exponent function

$$\beta^*(z) = (z - z_c)D(z) = (z - z_c)\frac{d}{dz} \ln F(z) = \sum_{n=0} b_n z^n. \tag{7.4}$$

This function must approach β as $z \to z_c$; hence estimates for β may be found by evaluating direct approximants $[L/M]_{\beta^*}$ to the b_n sequence *at* $z = z_c$. In practice one often modifies this method by replacing z_c in (7.4) by some reliable estimate $\tilde{z}_c$. In this case, however, the estimates for β will be biased by the choice of critical point estimate; this normally results in a fairly strong linear correlation between the estimates $\tilde{\beta}$ and $\tilde{z}_c$.

Some results of this technique are displayed in Table IV, which contains estimates for β derived from the magnetization series for the three-dimensional Ising model, by using the critical points estimated from the high temperature susceptibility series. (As a matter of fact, the estimates of T_c obtained independently from the low temperature series agree with these values to within better than one part in 10^3.) From Table IV we see that even the highly irregular expansion exhibited in Table II yields an almost constant sequence. A detailed investigation reveals that one has successfully penetrated analytically past four closer, nonphysical singularities. More impressive from the viewpoint of physical theory, is the agreement between the estimates for different lattices (involving, in each case, a continuation past a different pattern of nonphysical singularities). This evidence, and later work, indicates a universal value, $\beta = 0.312^{+0.003}_{-0.008} \simeq 5/16$, for all three-dimensional Ising lattices. This differs strongly from the exact two-dimensional result, $\beta = 1/8$ [see (4.5)], which exphasizes the importance of dimensionality in determining the values of critical exponents. Again, agreement with experiment is striking: neutron diffraction experiments on beta brass yield $\beta = 0.305 \pm 0.010$ [15]. These successes, and those obtained by the ratio technique, remain, so far, unduplicated by any other theoretical methods, and have established a dominant role for the series expansion approach in the study of critical point phenomena [6], [7], [11].

When the values of $z_c = 1/\mu$ and β are known, or reliably estimated, one can form direct approximants to the amplitude function

$$C(z) = (1 - \mu z)^{-\beta} F(z) = \sum_{n=0} c_n z^n, \tag{7.5}$$

which should converge well even in the vicinity of $z = z_c$. The original function can then be approximated well by

$$F(z) \simeq [L/M]_{C(z)} (1 - \mu z)^{\beta}. \tag{7.6}$$

Other variants are possible and have been explored. If the exponent β is known, the critical point may be estimated by studying the zeros (or poles if $\beta < 0$) of direct approximants to

$$G(z) = [F(z)]^{1/\beta} = \sum_{n=0} g_n z^n. \tag{7.7}$$

Sometimes the modified exponent function

$$E(z) = \left[\frac{d}{dz} \ln \frac{dF}{dz} \right] \Big/ \left[\frac{d}{dz} \ln F \right]. \tag{7.8}$$

which approaches $1 - (1/\beta)$ as $z \to z_c$, may be useful since the resulting exponent estimates are less closely correlated with the estimate for z_c than those found with the formula (7.4).

Finally some of the drawbacks of present Padé approximant techniques should be mentioned. Even when successive approximants converge well, the detailed nature of the approach to a limit can be quite irregular, and experience has shown that one often cannot gauge reliably the "trend" of the approximant values. Typical signs of this 'noisiness' can be seen in Table IV — note in particular the erratically high entry of 0.373 in the first fcc column. Another symptom of this same difficulty is the quite frequent appearance of 'tears' or "defects," that is a close pole-zero pairs, in a region of the complex plane which may be known to be free of singularities, and where other approximants appear well converged. Further mathematical progress concerning the rate of convergence of Padé approximants near singularities might help in understanding these phenomena. In the meanwhile, the ratio method, which converges in a more regular and well-understood manner, is often to be preferred in those circumstances where it can be employed.

Another feature of Padé approximant techniques is the difficulty of estimating weak singularities, i.e., those with small exponents such as near-logarithmic functions. This can be seen by first noting that Padé approximants are emphatically *not* invariant under the transformation (6.15) with a nonzero background, $k(z)$. On the contrary, changes in the first one or two coefficients of a long series can sometimes have quite disturbing effects on the values of high order approximants. This feature, of course, contrasts strongly with ratio techniques. The origin of the difficulty can be understood by considering a function such as

$$F(z) = A(z) \ln (1 - \mu z) + B(z), \tag{7.9}$$

[which has the same asymptotic form as (3.7) when $z \to 1/\mu$]. Differentiation introduces a simple pole but, unless $A(z)$ is constant, a logarithmic term still remains. Likewise, if a logarithmic derivative is taken, before or after differentiating $F(z)$, the correction term $d \ln C(z)/dz$ in (7.2), is still nonanalytic at $z = z_c$. For nonzero $B(z)$ this is still true if $\ln(1 - \mu z)$ is replaced by $(1 - \mu z)^{\beta}$ with, say, $|\beta| < 1$. Consequently, the Padé approximants must still attempt to represent a branch cut running from $z = z_c$, and so convergence will be impeded. (One may, however, sometimes be lucky in that the required discontinuity across the cut is small, so that fair convergence is obtained.)

8. **Conclusions.** In this brief review I have tried to show how simple but subtle numerical techniques, known in essence for over a hundred years, have had a profound effect in one of the most difficult areas of modern mathematical physics. The extensive work on the theory of

critical phenomena by no means exhausts the range of significant applications of the series expansion approach combined with the ratio and Padé approximant techniques (see, e.g., [2], [17]-[20]). We may look forward to a growing appreciation and application of these methods in fields where the nature of a singularity plays a central role.

As regards the theory of Padé approximants themselves, I have indicated how knowledge of the rate and nature of convergence, especially near a singularity, could be most helpful in practical applications. Another, perhaps easier task for the future, is to develop and test effective approximation schemes for handling power series expansions in two (or even more) variables. Experience in the area of critical point theory may be useful here, since, in certain cases, the singularity structure of a function $F(x, y)$ of physical significance, may be expected to have the so-called "scaling form" found to describe the free energy as a function of two thermodynamic variables, such as H and T (see [7] and [11]).

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Baker Laboratory, Cornell University, Ithaca, New York 14850

TABLE I

Susceptibility Expansion Coefficients a_n, for the square and simple cubic lattices, together with the numbers c_n of n-step self-avoiding walks (from Refs. [7], [13], [14])

Lattice	square ($d=2$)		simple cubic ($d=3$)	
n	a_n	c_n	a_n	c_n
1	4	4	6	6
2	12	12	30	30
3	36	36	150	150
4	100	100	726	726
5	276	284	3510	3534
6	740	780	16710	16926
7	1972	2172	79494	81390
8	5172	5916	375174	387966
9	13492	16268	1769686	1853886
10	34876	44100	8306862	8809878
11	89764	120292	38975286	41934150
12	229628	324932	182265822	198842742
13	585508	881500	852063558	943974510
14	1486308	2374444	3973784886	4468911678
15	3763460	6416596	18527532310	21175146054
16	9497380	17245332	86228667894	100117875366
17	23918708	46466676	401225391222	
18	60080156	124658732		

TABLE II

Series Expansion in Powers of $x = e^{-2K} = \exp(-2J/k_B T)$, for the spontaneous magnetization of the face centered cubic ($d = 3$) Ising lattice. (Further coefficients are known!)

$$\begin{aligned} M_0(T) = 1 &- 2x^{12} - 24x^{22} + 26x^{24} + 0 + 0 - 48x^{30} \\ &- 252x^{32} + 720x^{34} - 438x^{36} - 192x^{38} \\ &- 984x^{40} - 1008x^{42} + 12924x^{44} - 19536x^{46} \\ &+ 3062x^{48} - 8280x^{50} + 26694x^{52} + 143536x^{54} \\ &- 507948x^{56} + 406056x^{58} - 79532x^{60} \\ &+ 729912x^{62} + 631608x^{64} - 9279376x^{66} + \cdots \end{aligned}$$

TABLE III

Poles and Residues of $[M/M]$ Padé Approximants, to the logarithmic derivatives of the Ising model susceptibility series of Table I (after Ref. [4]). (Note that further entries can now be computed.)

Square			Simple cubic		
M	$(v_c)_{est}$	γ_{est}	M	$(v_c)_{est}$	γ_{est}
3	0.4093	1.626	2	0.2151	1.205
4	0.4164	1.797	3	0.2189	1.281
5	0.4121	1.682	4	0.21815	1.2505
6	0.41412	1.746	5	0.21818	1.2518
7	0.4142106	1.7496			
exact values	0.4142135 · · ·	1.7500	ratio estimates	0.21815	1.250

TABLE IV

Estimation of the Spontaneous Magnetization Exponent, from direct approximants to the exponent function $\beta^*(z)$ derived from data in Table II and Ref. [5]. Diagonal $[M/M]$, and next-to-diagonal sequences are presented.

Simple cubic			Body-centered cubic			Face-centered cubic		
M	β_{est}		M	β_{est}		M	β_{est}	
4	0.304	0.301	6	0.303	0.285	9	0.307	0.307
5	0.304	0.303	7	0.308	0.305	10	0.309	0.308
6	0.278	0.302	8	0.307	0.310	11	0.306	0.308
7	0.314	0.307	9	0.316	0.340	12	0.306	0.306
8	0.314	0.301	10	0.316	0.316	13	0.306	0.306
9		0.310	11	0.315	0.324	14	0.373	0.305
			12	0.313	0.313	15	0.309	0.306
			13	0.314	0.314	16		0.315

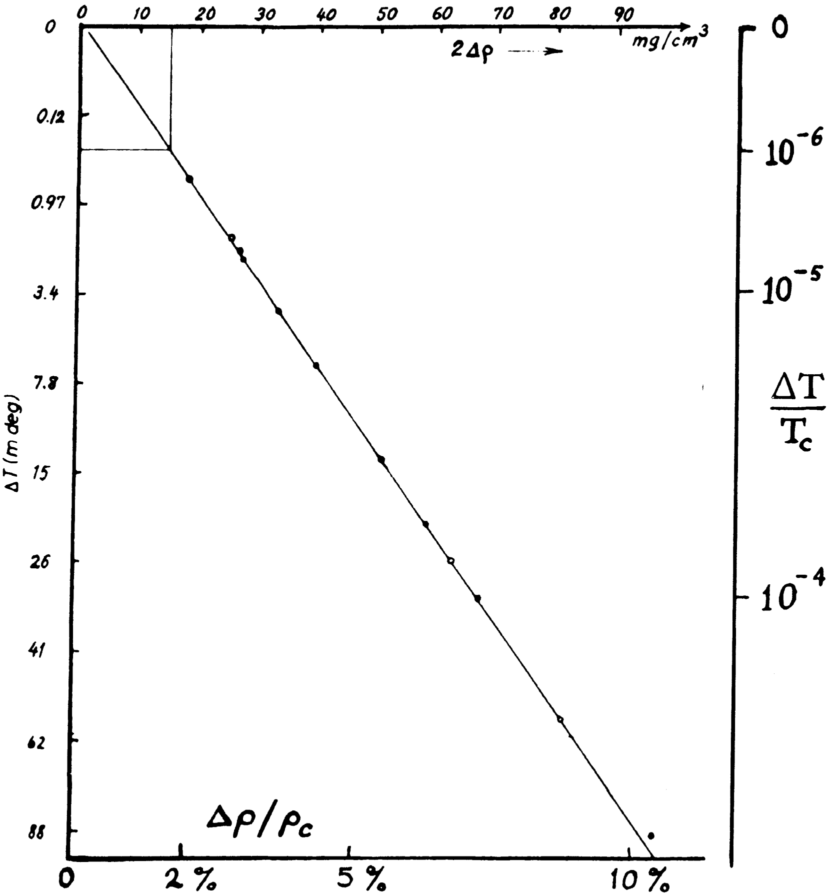

Figure 1. The coexistence curve of carbon dioxide close to the critical point, showing the variation of the density discontinuity $\Delta\rho(T)$ with temperature deviation $\Delta T = |T - T_c|$. The temperature scale is nonlinear, the ordinate of the graph being proportional to $(\Delta T/T_c)^{1/3}$. (After Lorentzen [**10**].)

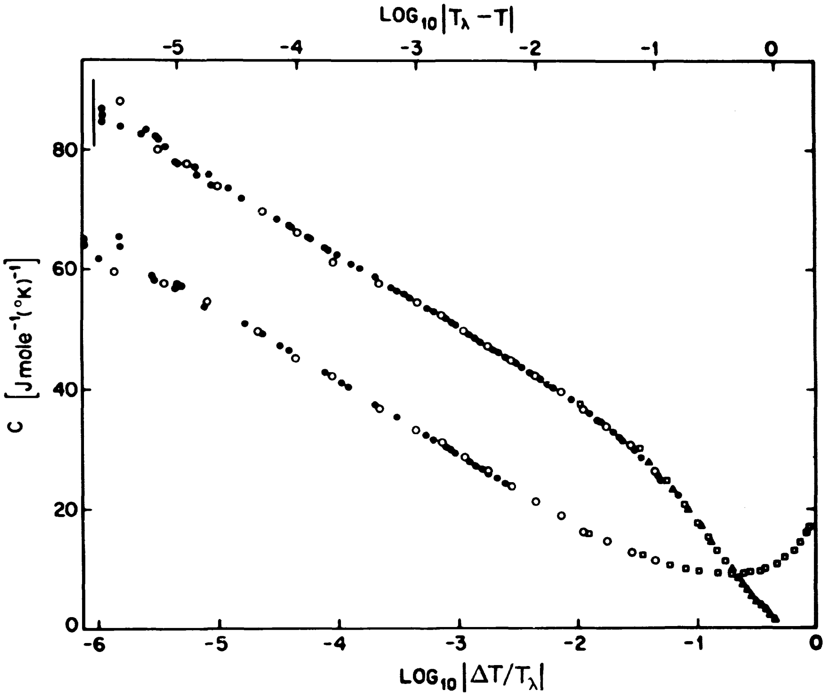

Figure 2. The specific heat, $C(T)$, of helium near the superfluid transition. Note that $C(T)$ is plotted linearly versus $\log_{10}(\Delta T/T_c)$ where $\Delta T = |T - T_\lambda|$ $(T_\lambda = T_c)$. The upper and lower curve apply for $T \gtrless T_c$, respectively. (After Ahlers [11].)

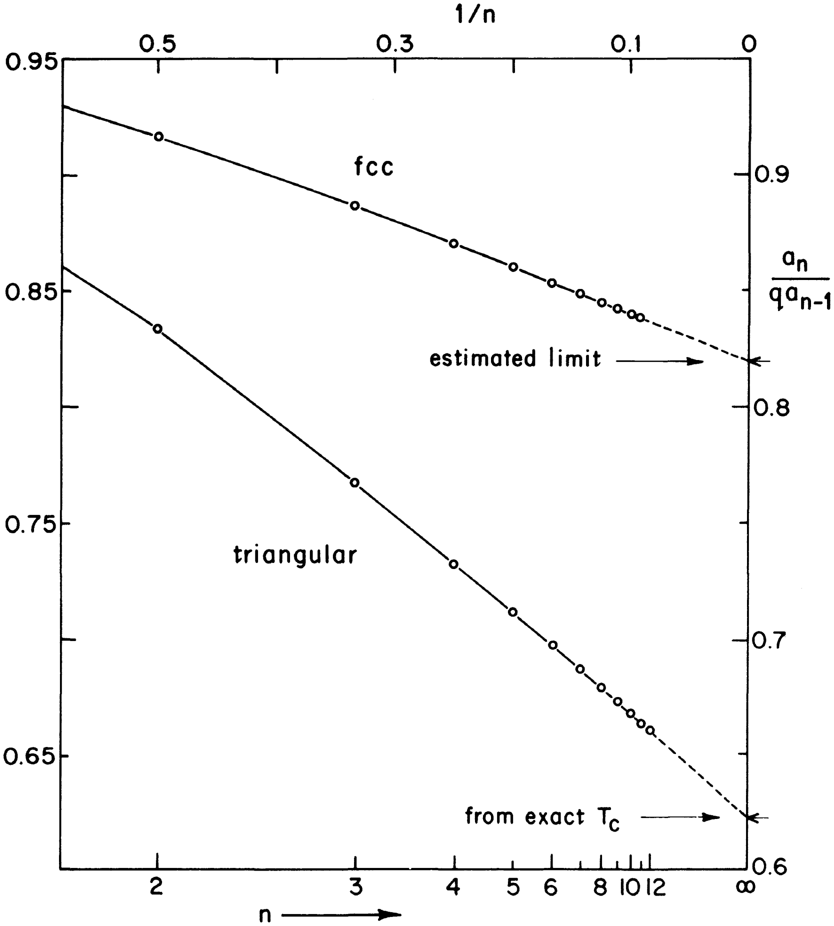

Figure 3. Plot of the ratios of coefficients a_n (normalized by the coordination number q) versus $1/n$ for the Ising model susceptibility series of the triangular ($d = 2$), and face centered cubic lattice ($d = 3$). Further data confirm the linear behavior.