

Thermodynamics Of Critical Points

There is in general no accurate theoretical description of the behavior of a system as it passes through its critical point. Current work, both experimental and theoretical, attempts to provide a unified theory that will be applicable to many different kinds of phase transition.

by Cyril Domb

NEW EXPERIMENTAL TECHNIQUES have been joined by novel theoretical approaches to give great impetus to the study of phase transitions. The systems studied include vapors near their critical points, ferromagnets near their Curie temperatures, antiferromagnets near their Néel points and the superfluid transitions. All these phase transitions, although apparently very different, show surprising similarities in their behavior near the critical point.

Experimentally the difficulties arise from the measurement of quantities that vary rapidly with temperature, necessitating fine control over the long times that the systems need to reach equilibrium.

Care must be taken to use materials of very high purity, and even gravitational forces may exercise a marked influence. The new techniques include improved resonance and calorimetric methods and the use of newly discovered ferromagnets with Curie temperatures located more conveniently for precise measurement than

was the case with those available earlier.

Theoretical physicists, after making little progress with general methods of approach initiated some 30 years ago, have turned to series-expansion methods that apply to various special cases. The interplay between theory and experiment has been stimulated by efforts to find a unified description of all critical phenomena.

General references only will be quoted here because the recent review articles by Leo Kadanoff and others,¹ Michael Fisher² and Peter Heller³ are comprehensive surveys that provide many individual references.

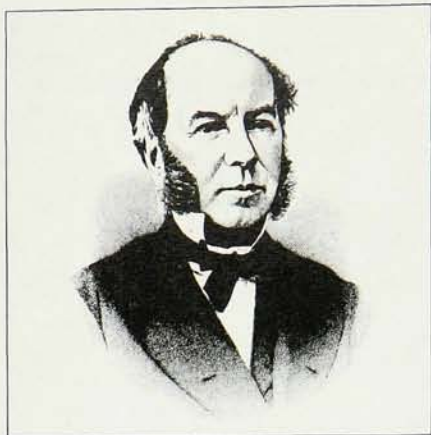
Van der Waals's law

The existence of a liquid-gas critical point was first established by Thomas Andrews in 1869 in his pioneering experiments on carbon dioxide. Only three years elapsed before Johannes van de Waals provided a plausible theoretical explanation of the experimental results, basing his derivation

on the concept of finite-sized molecules with long-range attractive forces. Van der Waals used Rudolf Clausius's virial theorem to calculate the change in pressure due to these forces. If we assume that the range of the attractive forces is long compared with the mean



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THOMAS ANDREWS (1813-1885) who discovered the existence of critical points in 1869. Van der Waals's theory followed three years after Andrew's experimental work with carbon dioxide.

free path, the modification in pressure is proportional to the square of the density. The finite size of the molecules was treated empirically; the volume V was replaced by $(V-b)$. Hence van der Waals arrived at the well known equation of state

$$P = -a/V^2 + RT/(V - b) \quad (1)$$

It is interesting that James Clerk Maxwell, who reviewed van der Waals's thesis in *Nature* in 1874, was quite happy about the treatment of the attractive term but critical of the repulsive contribution. In a similar vein Ludwig Boltzmann commented that "unfortunately van der Waals had to abandon mathematical rigor at a certain point in order to carry out his calculations." However, both were surprised and impressed with the agreement with experiment.

In the critical region van der Waals's

formula (supplemented by Maxwell's construction for the horizontal isothermal) predicts the behavior summarized in the box on this page.

Joseph Mayer's theory of condensation, which provided rigorous formulas for virial coefficients in terms of intermolecular forces, substantiated the criticism of Maxwell and Boltzmann. The repulsive term in the van der Waals formula could only be justified in the dilute gas region. It was realized by now that the attractive forces were much shorter ranged; how the formula furnished a qualitative description of condensation remained a mystery.

In magnetism John Hopkinson in 1890 was the first to note the disappearance of the ferromagnetic properties of iron at sufficiently high temperatures. More detailed experimental investigations of the behavior of ferromagnets were carried out by Pierre Curie and his collaborators from 1895 onwards. The brilliant suggestion by Pierre Weiss in 1907 that ferromagnets are characterized by a large internal field led to a theory that appeared capable of explaining all the experimental observations. The magnetic equation of state in this theory is

$$M/Nm = L[\beta m(H + aM)] \quad (3)$$

(M = magnetization, m = magnetic moment of each atom, a = constant of internal field, $L(x)$ = Langevin function = $\coth x - 1/x$, $\beta = 1/kT$). It gives rise to a nonzero spontaneous magnetization M_0 for temperatures less than the Curie temperature T_c , and to a magnetic susceptibility that becomes infinite as T_c is approached from the high-temperature side. The box on page 25 is a summary.

The analogy between equations 2 and 4 is striking although its significance was appreciated only at a much later stage. The final formula 4d also has an analog in the compressibility of the fluid along the critical isochore.

Resistivity and specific heat

To explain observed changes in resistivity in certain alloys G. Tammann suggested in 1919 that at sufficiently low temperatures atoms segregate into regular positions. This hypothesis was first confirmed experimentally by C. H. Johansson and J. O. Linde in 1925 by the observation of additional "superlattice" lines in x-ray photographs. In 1926 Tammann and O. Heusler observed an anomalous specific heat in beta brass at a particular temperature, and similar results were observed for other alloys by other experimenters. In the following years several attempts were made to interpret the above phenomena theoretically; these attempts culminated in the treatment by Lawrence Bragg and E. J. Williams in 1934 that centered around the important new concept of "long-range order." The parameter S that characterizes this quantity measures correlation between the occupation of lattice sites a large distance apart; when it is zero, there is no correlation. Bragg and Williams suggested that a superlattice is associated with a non-zero value of S and that T_c could be regarded as the temperature at which S becomes zero. The detailed behavior near T_c was predicted to be

$$S \approx \sqrt{3(1-t)} \quad (t \lesssim 1) \quad (5a)$$

$$= 0 \quad (t > 1)$$

$$\text{Specific heat } C_V \approx (3/2)R \quad (t \lesssim 1) \quad (5b)$$

$$= 0 \quad (t > 1)$$

Bragg and Williams noted the analogy with the Weiss theory of magnetism. Shortly afterwards the theory was improved by Hans Bethe and Rudolf Peierls to take account of short-range ordering.

In fact the problem of short-range ordering in fluids had been tackled many years before (in 1916) by L. S. Ornstein and F. Zernike who had introduced the pair-correlation function $g(R)$ of two particles of fluid separated by a distance R . They suggested with plausible arguments that in the critical region this function should be of the form

Pressure, volume and temperature relationships near the critical region, as predicted by van der Waals's formula

$$\text{Liquid-vapor coexistence curve } v_{\text{gas}} - v_{\text{liquid}} \approx 4(1-t)^{1/2} \quad (t \lesssim 1) \quad (2a)$$

$$\text{Critical isotherm } (p-1) \approx \frac{3}{2}(1-v)^3 \quad (t = 1) \quad (2b)$$

$$\text{Specific heat along critical isochore } c_v - \frac{3R}{2} \approx \frac{9}{2}R \quad (t \lesssim 1) \quad (2c)$$

$$= 0 \quad (t > 1)$$

where $p = P/P_c$, $v = V/V_c$, $t = T/T_c$

$$g(R) \approx (1/R) \exp[-AR(t-1)^{1/2}] \quad (6) \\ (t \gtrsim 1)$$

As the critical point is approached, the range of correlation becomes large, and this change causes large fluctuations in the scattering of light; hence an interpretation of the phenomenon of critical opalescence was provided. The analogy between the work of Ornstein and Zernike and ordering in alloys and magnets provided one of the fruitful developments of the past few years.

Improvement in low-temperature experimental techniques led to the discovery of further specific-heat anomalies apparently similar to equations 2c, 4c and 5b. W. H. Kessom (following earlier experiments of Heike Kamerlingh Onnes) showed that the onset of superfluidity in liquid helium and of superconductivity in metals are accompanied by such anomalies. Franz (later Sir Francis) Simon found similar behavior in solid ammonium chloride. The characteristic shape of the specific heat anomaly led to the term "lambda-point transition."

In 1933 Paul Ehrenfest attempted a thermodynamic description of these "higher-order transitions" in terms of the degree of contact between the Gibbs functions of the high- and low-temperature "phases." But the theory of second-order transitions ran into difficulties and could only be maintained by the assumption that some feature of the low-temperature phase

prevented it from continuing for $T > T_c$. Lev Landau then suggested a general mechanism that would account for this behavior. Systems with such specific-heat anomalies could be characterized by an "order parameter" η similar to the Bragg-Williams parameter S . If the free energy is expanded in powers of η on both sides of T_c , Landau showed that for a second-order transition the behavior of η is similar to S in equation 5a.

The Ising model

Because of the analogies in critical behavior between the various phenomena described above it is not surprising to find that one model can be used as an approximation to all of them. The Ising model (suggested by Wilhelm Lenz to his student Ernst Ising in 1925) allows each magnetic spin on a regular crystal lattice to take on two orientations, parallel or antiparallel to an external magnetic field H (energies $\mp mH$). Neighboring parallel spins have interaction energy $-J$, antiparallel spins $+J$. The Ising model provides a reasonable description of ferromagnetism for systems with extreme magnetic anisotropy. When J is less than 0 it serves as a model of order-disorder transitions. If one orientation of the spin is identified with a particle and the other with a hole, a crude description is available of liquid-vapor equilibrium ("lattice-gas" model).

In 1928 Werner Heisenberg ex-

plained in quantum-mechanical terms the origin of the Weiss internal field. He proposed a model in which magnetic spins in the lattice interacted by means of a vector coupling (corresponding to magnetic isotropy). The thermodynamic properties of the Weiss theory can be rederived for the Ising and Heisenberg models by reinterpreting the "internal field" as the mean field acting on any spin because of interaction with its neighbors. This description is now called the "mean-field approximation." We might expect it to be valid when the number of neighbors interacting with any spin is large enough that fluctuations can be ignored.

Onsager's exact solution

In 1944 Lars Onsager published his exact solution of the two-dimensional Ising model in zero field. In the following few years a number of important additional properties were calculated, particularly the spontaneous magnetization (or long-range order) and the correlation between pairs of spins separated by various distances. The results differ completely from the predictions of the classical theory. The specific heat is logarithmically infinite both above and below T_c ; the spontaneous magnetization approaches zero with a one-eighth-power law; and the pair correlation function is of the form

$$g(R) \approx R^{-1/4} \exp[-BR(t-1)] \quad (6a) \\ (t \gtrsim 1)$$

instead of

$$g(R) \approx (\log R) \exp[-B'R(t-1)^{1/2}] \\ (t \gtrsim 1) \quad (6b)$$

which is the same as the Ornstein-Zernike function in two dimensions. The results were also in apparent disagreement with experimental observations.

This exact theoretical work raised two fundamental questions. Was the classical theory completely discredited, or could some significance be attached to its qualitative description of critical behavior? Was the two-dimensional nature of the solution responsible for the difference between theory and experiment, or was the model itself inadequate as a representation of interactions in real substances?

The answer to the first question has

Behavior of a ferromagnet near the Curie point, as predicted by Weiss's theory

$$\text{Spontaneous magnetization } \frac{M_0}{m} \approx \frac{\sqrt{15}}{3} (1-t)^{1/2} \quad (t \lesssim 1) \quad (4a)$$

$$\text{Critical magnetization isotherm } \beta m H \approx \frac{9}{5} M^3 \quad (t = 1) \quad (4b)$$

$$\text{Specific heat } (H = 0) \quad c_H \approx \frac{5R}{2} \quad (t \lesssim 1) \quad (4c) \\ = 0 \quad (t > 1)$$

$$\text{Magnetic susceptibility } (H = 0) \quad \chi_0 \approx \frac{1}{3} \beta m (t-1)^{-1} \quad (t > 1) \quad (4d)$$

where $t = T/T_c$

recently been supplied, and classical theory has been vindicated. The Weiss and Bragg-Williams theories provide valid solutions for forces of very long range

$$\lim_{\epsilon \rightarrow 0} [\epsilon J \exp(-\epsilon R)] \quad (7)$$

representing the interaction between atoms separated by a distance R . Van der Waals's equation 1 is also valid for forces of the form of expression 7, (with a hard-core repulsion) but only in a one-dimensional system.

In higher dimensions the correct hard-sphere virial coefficients must be used; so Maxwell's and Boltzmann's criticism was well founded.

Series expansions

The answer to the second question requires a longer discussion and depends on the provision of reliable information about the behavior of three-dimensional models. Shortly after Onsager's work hopes were raised regarding the possibility of an exact solution in three dimensions. They diminished

steadily as the complex nature of the mathematical problem became manifest. In the absence of an exact solution two alternative lines were pursued by theoretical physicists; they were to improve the approximations and to develop exact series expansions at high and low temperatures.

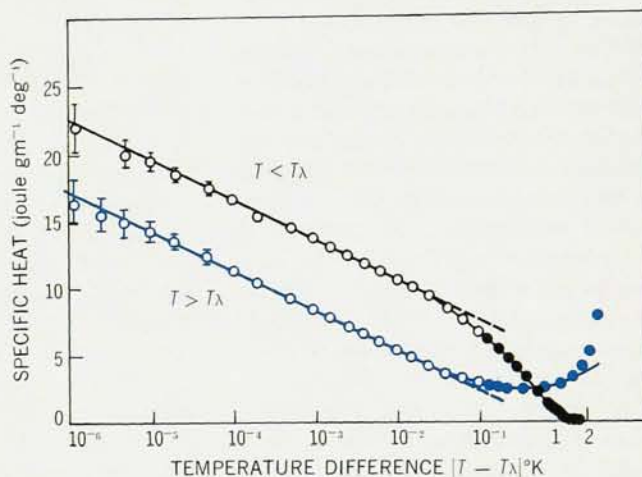
Considerable ingenuity was used to devise new and better approximations, but nearly all of them repeated the classical behavior in the critical region. Series expansions, however, did offer better prospects for an estimation of critical behavior when they were combined with physical insight. For example if expansions in inverse powers of temperature are made for magnetic susceptibility, the coefficients appear to remain positive. For the face-centered cubic lattice the coefficients are

$$\begin{aligned} \frac{kT\chi_0}{m^2} = & 1 + 12w + 132w^2 + 1404w^3 \\ & + 14\,652w^4 + 151\,116w^5 \\ & + 1\,546\,332w^6 + 15\,734\,460w^7 \\ & + 159\,425\,580w^8 + \dots \end{aligned} \quad (8)$$

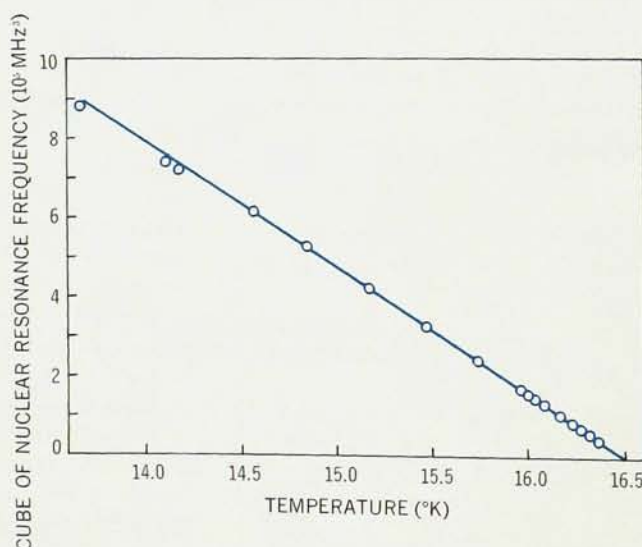
where $w = \tanh \beta J$.

Numerical analysis indicates that they settle down to a regular pattern, which makes it possible to guess their asymptotic behavior. The exact two-dimensional solutions could be used as a guide to the feasibility of these conjectures. In this way it was suggested that critical behavior of magnetic susceptibility is of the form $(t-1)^{-7/4}$ in two dimensions and $(t-1)^{-5/4}$ in three dimensions. (This second derivative of partition function with respect to magnetic field had not been calculated exactly in two dimensions; it is related to the pair-correlation function, and the expression above subsequently received rigorous justification.)

Some of the series derived at low temperatures are not consistent in sign, and it proved to be more difficult to make any precise estimate of critical behavior in this case. If the function we are seeking is of the form $(1+3t)^g(1-t)^h$, its power-series expansion will be dominated by the first spurious singularity that corresponds to a negative temperature. Here the introduction of the Padé approximant represented a major step forward. This method of analytic continuation was introduced by H.



ACCURATE MEASUREMENTS of the specific heat of liquid helium as a function of $\log |T - T_\lambda|$. The solid lines represent an empirical relation $4.55 - 3.00 \log_{10} |T - T_\lambda| - 5.20\Delta$, where $\Delta = 0$ for $T < T_\lambda$, $\Delta = 1$ for $T > T_\lambda$. —FIG. 1



TEMPERATURE DEPENDENCE of the cube of the Eu^{153} nuclear-resonance frequency between 13.6 and 16.33°K. In this range the law $M_0 \propto D(1-t)^{1/2}$ is obeyed for EuS . —FIG. 2

Padé in 1892 and appears to have been dormant since then except for those mathematicians concerned with continued fractions. It enables the dominant singularity to be bypassed and attention to be focused on the singularity of physical importance. It was conjectured that spontaneous magnetization in the critical region is of the form $(1 - t)^{5/16}$ for a three-dimensional model.

It was found useful to use the concept of "mean range of order" L defined by

$$L^2 = \int R^2 g(R) dR / \int g(R) dR \quad (9)$$

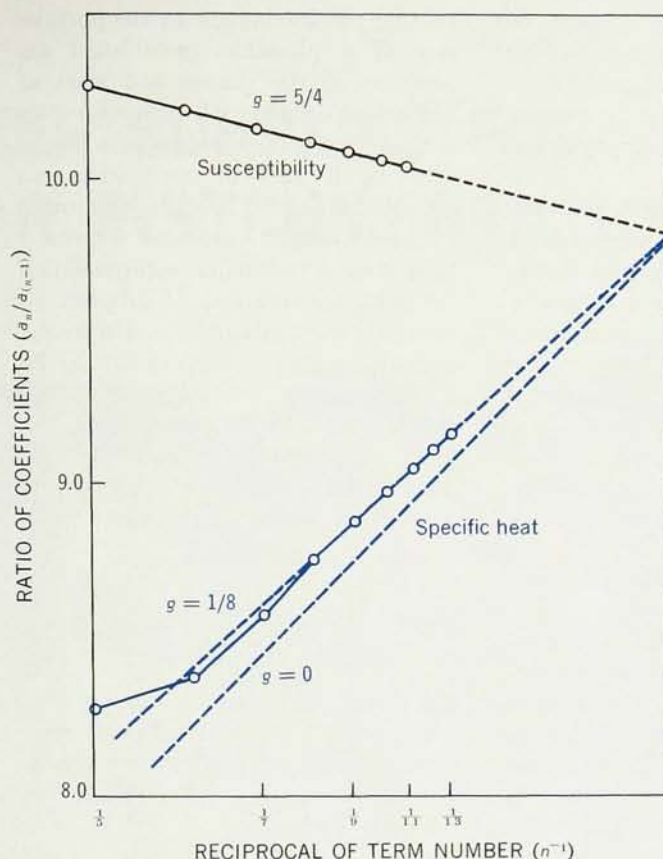
to calculate the pair-correlation function in the critical region. L behaves as $(t - 1)^{-1/2}$ in the Ornstein-Zernike approximation and as $(t - 1)^{-1}$ in the Onsager solution. The behavior in three dimensions was $(t - 1)^{-\nu}$ with ν approximately equal to 0.645.

For the Heisenberg model the derivation of series expansions is more difficult, and the critical region is less explored. Early analysis proposed $(t - 1)^{-4/3}$ ($t > 1$) for the magnetic susceptibility. Subsequent calculations indicate a somewhat larger index.

A word should be added about the mathematical and technical problems that arise in the derivation of series expansions. The coefficients involve the number of possible linear graphs of l lines that can be constructed from l bonds of the lattice (termed "lattice constants"). A variety of methods has been used to calculate these quantities and to ensure that the results are free from error. Recently computers have been effectively introduced, but the problems are novel in character and cannot be handled by standard programs. Progress has been greatest where there is a suitable synthesis of mathematical analysis and computer facility.

The experimental situation

It was realized many years ago that although experimental data on the liquid-vapor-coexistence curve conforms reasonably well to a law of corresponding states, the behavior near T_c does not follow the square law predicted by van der Waals; it fits a cube law quite closely. Accurate experiments in the early 1950's confirmed this behavior and also showed



CONJECTURED ASYMPTOTIC BEHAVIOR compared with exact series-expansion calculations in the three-dimensional Ising model. This work, by M. F. Sykes, is for the face-centered-cubic lattice. Ratios $a_n/a_{(n-1)}$ of the n th and $(n - 1)$ th coefficients of expansions, in powers of $\tanh(J/kT)$, of susceptibility and specific heat are plotted as functions of $1/n$. These plots become linear for large n ; the slopes determine the critical index g . The straight lines cut the ordinate at a point that determines the critical temperature. —FIG. 3

that the critical isotherm disagrees with the van der Waals prediction. The index was estimated as 4.2.

Similarly early experiments on ferromagnets recorded derivations from the linear Curie-Weiss law for reciprocal of magnetic susceptibility as a function of $(T - T_c)$. A distinction was made between "paramagnetic" and "ferromagnetic" Curie temperatures to take these deviations into account.

The impact of Onsager's solution on experimental research was first manifested in the accurate measurement of the specific heat of liquid helium near the lambda point, which established the logarithmic nature of the singularity (figure 1). Thereafter several transition points in magnetic salts were

investigated and found to be similar in behavior. A specific-heat discontinuity of the second-order Ehrenfest type appeared to be the exception rather than the rule. In the 1960's Russian experimental workers made accurate measurements of the specific heats of argon, oxygen and nitrogen along a critical isochore. They interpreted their results in terms of a logarithmic infinity (although it was suggested subsequently that the results could be fitted equally well by a small-power law).

Nuclear magnetic resonance

A new accurate tool for measurements of the spontaneous magnetization of ferromagnets was nuclear magnetic resonance. This technique allows di-

rect observation of the field acting on a particular atom. Europium sulfide was found to be a ferromagnet ($T_c = 16.5^\circ\text{K}$), and its spontaneous magnetization near T_c fitted a $1/3$ power law accurately (figure 2).

Old data on the magnetic susceptibility of nickel at temperatures above T_c were examined again, and it was found that they conformed to a relation $(t - 1)^{-\gamma}$ with γ approximately equal to $4/3$. Previous analyses had attempted to fit the data by empirical relations for χ_0^{-1} of the form $a(t - 1) + b(t - 1)^2$. New and more accurate experiments confirmed this interpretation. Experiments on magnetic salts indicated similar behavior, but γ was smaller when the substance was magnetically anisotropic.

The technique of neutron diffraction furnished a new means of measuring order directly, and it was used extensively to measure correlation in magnetic substances. It could also be used for alloys, and measurements on beta brass showed reasonable agreement with predictions of the three-dimensional Ising model.

Finally measurements of specific heat of magnetic salts as they undergo lambda-point transitions are used to calculate the energy and entropy at the critical point. Comparison with theoretical estimates for the Ising and Heisenberg models (whichever appears appropriate for the particular salt) give encouraging agreement.

The answer to the question posed above on the applicability of different theoretical models can now be given with a fair degree of confidence. The disagreement of Onsager's solution with experiment is due to the two-dimensional character of the model. In three dimensions both the Ising and Heisenberg models can usefully be identified with interactions in real physical systems.

A unified treatment?

The series-expansion method treats each thermodynamic quantity separately and analyzes its critical behavior. We reasonably expect these quantities to be related, with thermodynamics alone imposing some restrictions. The first indication of relations between these quantities came from the "droplet model," which attempts to construct a mimic partition func-

tion for condensing gas by the postulation of a plausible geometrical description of the shapes and sizes of individual droplets. The model does not take account of "volume exclusion" (that is, the fact that no volume can be simultaneously occupied by more than one droplet). So we expect it to provide a reasonable approximation for low concentrations of droplets although some caution is needed in the critical region. Nevertheless the model predicts relations for critical behavior as T approaches T_c from below that are satisfied both by the two-dimensional Ising model and by the mean-field theory. They are

$$\alpha' + 2\beta + \gamma' = 2 \quad (10)$$

where $c_H \propto (1 - t)^{-\alpha'}$, $M_0 \propto (1 - t)^\beta$, $\chi_0 \propto (1 - t)^{-\gamma'}$, $t \lesssim 1$.

The discovery of these relations stimulated rigorous thermodynamic investigations, and it was found, for example, that under quite general conditions the inequality

$$\alpha' + 2\beta + \gamma' \gtrsim 2 \quad (11)$$

can be established.

One of the most attractive features of the Weiss theory of ferromagnetism is the unity of approach; from the single equation 3 the complete pattern of critical behavior can be deduced. Would it be possible to provide one such equation for the Ising or Heisenberg model from which all critical indices could be obtained? Such an equation of state has been proposed recently in the form

$$\beta m H = (t - 1)^\Delta F[H^{-1}(t - 1)^{\Delta - \gamma}] \quad (12)$$

This equation is not as complete as equation 3 and claims to represent only the dominant terms in the critical region. The function F is assumed to be analytic, and to vary from model to model, as do the parameters γ and Δ . (Even for the mean-field theory, equation 3 is valid only for classical vector spins, $s \rightarrow \infty$; for finite spin s the Brillouin function must be used).

The form of equation 12 is suggested by an analysis of critical behavior of higher derivatives of magnetization with respect to field H . The function F should have the property that all singularities disappear in a nonzero magnetic field. This assumption is believed to be valid generally

for models of ferromagnetism. Then a transition can be made from the region $T > T_c$ to the region $T < T_c$ as is done in classical theory.

The form 12 has been interpreted physically in terms of "scaling laws" in the critical region. Suppose the given macroscopic system is divided into subsystems. Then the original model can be replaced by a new model in which the original unit is replaced by a subsystem, and the original interaction is replaced by an interaction between subsystems. It is suggested that because of the long range of correlation near T_c the new model can be "mapped" on the original model. Hence an equation of state of the form in equation 12 can be derived.

If an equation of state of this type is accepted it follows that critical behavior depends on only two parameters; if the critical behavior of two thermodynamic quantities is known, the behavior of the remainder can be deduced. For example, from the values $\gamma = 5/4$, $\beta = 5/16$ for the three-dimensional Ising model we can show that the specific heat behaves as $(t - 1)^{-1/8}$.

The possibility of such a unified approach has given great impetus to theory and experiment to test the validity of the relations it proposes. For the three-dimensional Ising-model evidence from extended high-temperature series provides strong support for the prediction of the exponent $-1/8$ (figure 3). Further work is required to test the low-temperature predictions and to deal with the Heisenberg model. Naturally a greater challenge is to find a more substantial basis for these relations and indeed for the whole pattern of critical behavior that has emerged.

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