Equation of State Near a Critical Point

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A quantitative phenomenological approach to the thermodynamics of critical phenomena is proposed. The equation of state and all the thermodynamic quantities are expressed in terms of a function which does not have singularities in the critical region and which can be expanded in a rapidly converging series in powers of a certain effective order parameter. If the first two terms of the expansion are retained, as in the Landau theory, one obtains an equation of state which describes the experimental data to within 5–10% accuracy. Allowance for the next term improves the agreement with experiment, but the remaining terms are insignificant at the present level of experimental accuracy.

INTRODUCTION

1. Numerous experimental data point to the fact that the equation of state of gases close to the critical point and the equation of state of ferromagnets close to the Curie point are analogous and possess a scaling property. For gases, the scaling hypothesis is usually formulated thus (cf., e.g., [1]):

$$\frac{P-P_c}{\tau^{\beta+\gamma}} = f\left(\frac{\rho-\rho_c}{\tau^\beta}\right). \tag{1}$$

Here, P is the pressure, ρ is the density, T is the temperature, and P_c, ρ_c and T_c are their critical values:

$$\tau = (T-T_c)/T_c.$$

The critical indices β and γ characterize respectively the critical isobar (coexistence curve of the phases):

$$|\rho-\rho_c| = B(-\tau)^\beta, \quad \tau<0, \quad P=P_c \tag{2}$$

and the temperature dependence of the isothermal compressibility:

$$(\partial\rho/\partial P)_T = C_\pm|\tau|^{-\gamma}, \quad \tau \gtrless 0, \quad P=P_c. \tag{3}$$

The coefficients B and $C_\pm$ in the scaling laws (2) and (3) are determined by the properties of the function f(x).

For ferromagnets, an analogous equation of state near the Curie point is assumed (cf. [1]):

$$H/\tau^{\beta+\gamma} = f(M/\tau^\beta), \tag{4}$$

where H and M are the magnetic field and magnetic moment per unit volume in the appropriate units, e.g., in units of the saturation field and saturation moment. The analog of the critical isobar (2) will be the dependence of the spontaneous moment on the temperature:

$$M = B(-\tau)^\beta, \quad \tau<0, \quad H=0, \tag{5}$$

and the analog of the scaling law (3) for the compressibility will be the scaling law for the susceptibility in zero field:

$$\chi = (\partial M/\partial H)_T = C_\pm|\tau|^{-\gamma}, \quad \tau \gtrless 0, \quad H=0. \tag{6}$$

Experiments give approximately the same values of the critical indices for ferromagnets and gases:

$$\beta \approx 0.35, \quad \gamma \approx 1.25 \tag{7}$$

with small variations for different systems.

In the following, we shall use the terminology for a ferromagnet, it being implied that we can go over to gases by making the replacement

$$H \leftrightarrow P-P_c, \quad M \leftrightarrow \rho-\rho_c, \quad \chi \leftrightarrow (\partial\rho/\partial P)_T.$$

In the classical theory, i.e., in the Curie-Weiss theory for ferromagnets and in the van der Waals equation for gases, the critical indices are

$$\beta_0 = 1/2, \quad \gamma_0 = 1, \tag{8}$$

and the function f(x) in (1) and (4) has the simple form:

$$f_0(x) = ax + bx^3. \tag{9}$$

2. The important fact that the experimental values of the indices 2β and γ (7) are not integers means that the equation of state must be considerably more complicated than the classical equation (9). Indeed, it follows from physical considerations that the equation of state should have no singularities in τ at $H \neq 0$, inasmuch as the magnetic field orders the spins, and the states for $\tau > 0$ and $\tau < 0$ cannot differ in their symmetry. For non-integer indices 2β and γ, this physical requirement leads to complicated behavior of the function f(x) as $x \to \infty$: [1]

$$f(x) \to \tilde{b}x^{(\beta+\gamma)/\beta} + \tilde{a}x^{(\beta+\gamma-1)/\beta} + \ldots, \quad x\to\infty. \tag{10}$$

In addition, the function f(x) should have Lee-Yang [2] singularities at imaginary x, so that states for $\tau < 0$ are obtained by analytic continuation of the function f(x) on to another sheet of the Riemann surface. [1]

All these complications have arisen only because we chose as the scale factor in formulating the scaling hypothesis (4) the unsuitable quantity τ, which goes to zero at the transition point and becomes negative below the transition point. We propose to circumvent these difficulties by the following device.

3. As the scale factor, we choose a positive-definite quantity—the susceptibility χ in finite field,

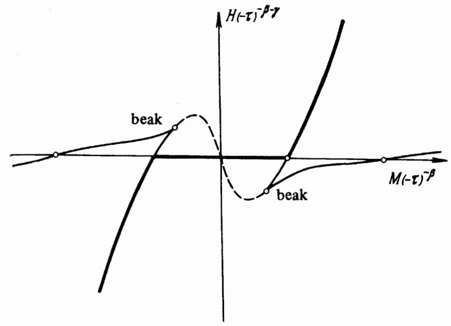
$$\chi = (\partial M/\partial H)_T > 0, \quad H \neq 0,$$

i.e., we shall formulate the scaling hypothesis thus:

$$H\chi^{(\beta+\gamma)/\gamma} = \varphi(M\chi^{\beta/\gamma}). \tag{11}$$

This relation connects H, M and $\chi = (\partial M/\partial H)_T$, i.e., is an implicit differential equation for the isotherms. The equation can be solved in general form and permits us to find a parametric equation of state, in which the function $\varphi(m)$ appears. After this, all observable quantities can be expressed in terms of the function $\varphi(m)$.

The advantage of this approach over the usual ap-



Qualitative form of the isotherm below the Curie point. The thick line is the stable branch, the thin lines are the metastable branches, and the dashed line is the self-consistent field-theory isotherm.

proach consists, as we shall see, in the fact that the function $\varphi(m)$ has very simple properties, analogous to the properties of the function $f_0(x)$ (9) in the classical theory, and can be expanded in a rapidly convergent series:

$$\varphi(m) = m + \varphi_3 m^3 + \varphi_5 m^5 + \ldots \tag{12}$$

Both the argument $m = M\chi^{\beta/\gamma}$ of the function $\varphi(m)$ and the function itself will turn out to be bounded quantities, $\leqslant 1$ in the whole critical region H, $\tau \to 0$, and the nearest Lee-Yang singularities correspond to an essential singularity of the function $\varphi(m)$ at infinity. If there are no other singularities, the function $\varphi(m)$ is an entire function.

The requirement that the equation of state be analytic as $\tau \to 0$ in finite field $H \neq 0$, which led to complicated properties of the function f(x) as $x \to \infty$, does not lead to the appearance of singularities of $\varphi(m)$, but gives a relation between the derivative $\varphi'(m_0)$ at the point m_0, where $\varphi(m_0) = \beta m_0/(\beta + \gamma)$, and the critical indices β and γ. This relation has the following striking form:

$$\beta + \gamma = \bar{n}/(\bar{n} - 1),$$

where the quantity

$$\bar{n} = \frac{m_0\varphi'(m_0) - m_0}{\varphi(m_0) - m_0}.$$

characterizes the convergence of the expansion (12); if the n-th term plays the main role, then $\bar{n} = n$.

If only the first two terms in the function $\varphi(m)$ are retained, as in classical theory, we obtain the relation $\beta + \gamma = 3/2$, which is fulfilled experimentally to within 5–10% accuracy. The equation of state in this case differs from the classical one, if $\gamma \neq 1$, and coincides with the empirical equation of the so-called linear model,[3] which describes with 5–10% accuracy the experimental data on critical points and Curie points. Taking account of the next term $\varphi_5 m^5$ in $\varphi(m)$ improves the agreement with experiment, while the contribution of the remaining terms is insignificant at the present level of experimental accuracy.

Interesting results are obtained for the metastable region. The isotherms for $T < T_c$ terminate not at the point where $(\partial M/\partial H)_T = \infty$, as do the van der Waals isotherms, but at the point where $(\partial^2 M/\partial H^2)_T = (\partial^2 H/\partial M^2)_T = \infty$. In the neighborhood of this point, the isotherm branches and resembles a beak. In addition, at sufficiently small τ, metastable states in which the spontaneous moment is several times greater than in the stable state are possible (see the figure).

I. EQUATION FOR THE ISOTHERMS AND ITS SOLUTION

In order to find the equation of state, we need to solve the differential equation (11) for the isotherms. This equation can be solved in general form, for arbitrary function $\varphi(m)$. We shall seek a solution in parametric form, as a function of the parameter m:

$$\chi = (\partial M/\partial H)_T = \chi(m, \tau),$$
$$M = m[\chi(m, \tau)]^{-\beta/\gamma}, \quad H = \varphi(m)[\chi(m, \tau)]^{-(\beta+\gamma)/\gamma}. \tag{13}$$

For a known function $\varphi(m)$, the problem reduces to determining the susceptibility $\chi(m, \tau)$. Making the replacement

$$\frac{\partial M}{\partial H} = \frac{\partial M}{\partial m} \Big/ \frac{\partial H}{\partial m},$$

we obtain for $\chi(m, \tau)$ the equation

$$\chi = \frac{\partial M}{\partial m} \Big/ \frac{\partial H}{\partial m} = \chi \frac{\gamma\chi - \beta m\, \partial\chi/\partial m}{\gamma\varphi'(m)\chi - (\beta+\gamma)\varphi(m)\,\partial\chi/\partial m}. \tag{14}$$

This equation reduces to a linear equation and is easily solved:

$$\chi(m,\tau) = \chi(0,\tau)\exp\left\{\gamma\int_0^m \frac{dm[\varphi'(m) - 1]}{(\beta+\gamma)\varphi(m) - \beta m}\right\}. \tag{15}$$

The formulas (13) and (15) solve the problem posed, i.e., that of determining the isotherms from the known function $\varphi(m)$. In order that the integral in (15) converge as $m \to 0$, it is necessary that $\varphi'(0) = 1$, since $\varphi(0) = 0$ and the denominator of the integrand is proportional to m as $m \to 0$. One can also arrive at the condition $\varphi'(0) = 1$ more simply, directly from Eq. (11). In order that the moment vanish like χH as $H \to 0$ above the transition point, it is necessary that $\varphi(m)$ behave like $\varphi'(0)m$ as $m \to 0$. Then non-integer powers of the susceptibility cancel on the left and right in (11) and we obtain $H \to \chi^{-1}M\varphi'(0) = \varphi'(0)H$, whence $\varphi'(0) = 1$.

II. EQUATION OF STATE IN STRONG AND WEAK FIELDS AND RELATION FOR THE INDICES

We now investigate the equation of state in strong and weak fields and express the susceptibilities above and below T_c, the moment in a strong field and the spontaneous moment in terms of the function $\varphi(m)$. We first consider the region $m \to 0$ in (13) and (15). In this case, as is easily seen,

$$M \to \chi(0, \tau)H \to 0.$$

This region corresponds to weak fields above the transition point. The susceptibility $\chi_+(\tau)$ is found to be equal to the quantity $\chi(0, \tau)$ in (15):

$$\chi(0, \tau) = \chi_+(\tau) = C_+\tau^{-\gamma}, \quad \tau > 0. \tag{16}$$

We now increase m. How does the function $\varphi(m)$ behave as we do this? First, it increases linearly, $\varphi(m) = m$, and then the terms $\varphi_3 m^3$ and $\varphi_5 m^5$ enter; these should lead to the result that $\varphi(m)$ begins to decrease and goes to zero at a certain $m = m_1$ such that there will be a spontaneous moment. However, before $\varphi(m)$ goes to zero, it intersects the straight line $\varphi = \beta m/(\beta+\gamma)$, so that the denominator in (15) goes to zero. We shall examine the neighborhood of the point of intersection

$$\varphi(m_0) = \beta m_0/(\beta + \gamma). \tag{17}$$

Near this point, the integral in (15) has a logarithmic singularity and the susceptibility $\chi(m, \tau)$ has the asymptotic form:

$$\chi(m, \tau) \to \text{const} \cdot \chi(0, \tau)(m_0 - m)^{\gamma\rho},$$

where we use the notation

$$\rho \equiv [\varphi'(m_0) - 1] / [(\beta + \gamma)\varphi'(m_0) - \beta].$$

When we try to increase m, the susceptibility $\chi(m, \tau)$ becomes complex, i.e., we fall into the unphysical region, if we keep $T > T_c$. But if we make $T \to T_c$ simultaneously with the passage $m \to m_0$, it can be arranged that $\chi(m, \tau)$ remain finite for $T = T_c$, $m = m_0$, and remain positive for $T < T_c$, $m > m_0$. Since $\chi(0, \tau) \propto \tau^{-\gamma}$, the connection between $m_0 - m$ and τ must be the following:

$$(m_0 - m)^\rho = \text{const} \cdot \tau \quad (\chi = \text{const} > 0).$$

If m and τ are connected by this relation, then the magnetic field H in (13) remains finite as $\tau \to 0$. The magnetic moment in (13) also remains finite and is proportional to $H^{\beta/(\beta+\gamma)}$.

The next term in the expansion of M in powers of τ will be proportional to $m_0 - m \propto \tau^{1/\rho}$. On the other hand, from analyticity considerations, we expect that the expansion in τ begins with the linear term. For this it is necessary that $\rho = 1$, i.e.,

$$(\beta + \gamma)\varphi'(m_0) - \beta = \varphi'(m_0) - 1.$$

Using Eq. (17) and the expansion (12), we can bring this relation to the striking form

$$\beta + \gamma = \bar{n} / (\bar{n} - 1). \tag{18}$$

Here the quantity

$$\bar{n} = \frac{3\varphi_3 m_0^3 + 5\varphi_5 m_0^5 + \ldots}{\varphi_3 m_0^3 + \varphi_5 m_0^5 + \ldots} \tag{19}$$

characterizes the convergence of the expansion (12); if the term with label k plays the main role, then $\bar{n} = k$.

These relations connect the critical indices β and γ with the function $\varphi(m)$ and guarantee that there is no singularity in the equation of state as $\tau \to 0$, $H \neq 0$. The physical meaning of this requirement is clear: the magnetic field orders the spins and there is no difference in the symmetry of the states at $\tau > 0$ and at $\tau < 0$; consequently, a second-order phase transition is impossible and there need be no singularity at $\tau = 0$. In the neighborhood of $\tau = 0$, $H \neq 0$, the equation of state can be written thus:

$$M = \chi_0^{-\beta/\gamma} m_0 + O(\tau), \quad H = \chi_0^{-(\beta+\gamma)/\gamma} \varphi(m_0) + O(\tau), \tag{20}$$

where χ_0 is the susceptibility at $\tau = 0$, $H \neq 0$. Eliminating χ_0, we obtain the scaling law for the moment M in a strong field:

$$M = DH^{\beta/(\beta+\gamma)}, \quad D = m_0[\varphi(m_0)]^{-(\beta+\gamma)/\beta}. \tag{21}$$

We now consider the next region $m > m_0$. This region corresponds to the state below T_c. With increasing m, we approach the point m_1 at which $\varphi(m)$ first goes to zero: $\varphi(m_1) = 0$. In the neighborhood of this point, the equation of state is as follows:

$$\begin{aligned} M &\to [\chi(m_1, \tau)]^{-\beta/\gamma} m_1 + \chi(m_1, \tau) H, \\ H &\to [\chi(m_1, \tau)]^{-(\beta+\gamma)/\gamma} \varphi'(m_1)(m - m_1). \end{aligned} \tag{22}$$

The quantity $\chi(m_1, \tau)$ is obtained by analytic continuation of the function (15) into the region $\tau < 0$, $m = m_1 > m_0$. As pointed out above, it can be arranged that $\chi(m, \tau)$ remain positive in this continuation, i.e., that we do not go outside the region of stability. In this case, the complex parts of the factors ($\chi(0, \tau)$ and the exponential) are mutually eliminated, as we saw above, i.e., $\chi(m_1, \tau)$ can be written thus:

$$\chi_-(\tau) = \chi(m_1, \tau) = C_+(-\tau)^{-\gamma} \exp\left\{\gamma \int_0^{m_1} \frac{dm(\varphi'(m) - 1)}{(\beta + \gamma)\varphi(m) - \beta m}\right\}. \tag{23}$$

The integral in (23) is to be understood in the sense of the principal value, i.e., as the real part of the integral in (15). The formulas (22) and (23) determine the spontaneous moment $M_0(\tau)$ and the susceptibility $\chi_-(\tau)$ below the transition point. They correspond to the laws (5) and (6) with the coefficients C_- and B equal to

$$C_- = C_+ \exp\left\{\gamma \int_0^{m_1} \frac{dm(\varphi'(m) - 1)}{(\beta + \gamma)\varphi(m) - \beta m}\right\}, \tag{24}$$

$$B = m_1 C_-^{-\beta/\gamma}, \tag{25}$$

where m_1 is the first root of the function $\varphi(m)$.

Now we shall increase m. The following interesting phenomena then occur. In the first place, H/M becomes negative for $m > m_1$. However, we still do not emerge from the region of stability, since $\chi > 0$. We simply reach the metastable branch of the isotherm H(M, T) (see the figure). On further increase of m, we reach the point m_c at which the numerator and denominator in (14), i.e., $\partial M/\partial m$ and $\partial H/\partial m$, go to zero simultaneously. This occurs for

$$(\beta + \gamma)\varphi(m_c) = \beta\varphi'(m_c) m_c.$$

In the neighborhood of this point,

$$\begin{aligned} M &= M(m_c) + a(m - m_c)^2 + b(m - m_c)^3 + \ldots, \\ H &= H(m_c) + c(m - m_c)^2 + d(m - m_c)^3. \end{aligned}$$

The isotherm bifurcates, having a continuous derivative $\chi^{-1} = (\partial H/\partial M)_T$ at the branch point, while the second derivative $(\partial^2 H/\partial M^2)_T$ goes to infinity. Then H and M increase, and if the function $\varphi(m)$ has one more zero, m_2, then the quantity H(M, T) goes to zero at $m = m_2$, i.e., there exists a metastable state with another spontaneous moment.

III. THE FREE ENERGY IN THE CRITICAL REGION

We now express the free energy of a ferromagnet in terms of the function $\varphi(m)$. The free energy is connected with the equation of state by the following obvious formula:

$$F(H, T) = \int_H^{H_0} M(H', T)\, dH' + F(H_0, T). \tag{26}$$

We shall choose the upper limit H_0 to be some constant, much greater than H and independent of T. Then $F(H_0, T)$ corresponds to a ferromagnet in a finite field and does not have a singularity at $T = T_c$. We are interested in the part that is singular as H, $\tau \to 0$; this is contained in the integral

$$F_{sing}(H, T) = \int_H^\infty M(H', T)\, dH'. \tag{27}$$

Here it is necessary to make the following remark.

The integral in (27) formally diverges at the upper limit. Indeed, for $H' \gg \tau^{\beta+\gamma}$, i.e., in a strong field, the moment $M(H', \tau)$ is determined by formula (23), and the contribution from the upper limit $H_0 \to \infty$ is as follows:

$$\int^{H_0} D(H')^{\beta/(\beta+\gamma)}\,dH' \to DH_0^{(2\beta+\gamma)/(\beta+\gamma)}\frac{\beta+\gamma}{2\beta+\gamma}.$$

Since β and γ are positive, this contribution, which is independent of H and τ, tends to infinity as $H_0 \to \infty$, i.e., the integral (27) diverges. This difficulty can be avoided by means of the following device. We shall consider the integral in (27) as an analytic function of the indices β and γ and shall define it for $\beta, \gamma > 0$ as the analytic continuation from the side $2\beta + \gamma < 0$, where the integral converges. It is easily seen that in the analytic continuation we lose only an unimportant regular contribution from the upper limit, but keep the singular part.

Substituting our parametric formulas (13) and (15) into (27) and proceeding to the integration over m ($dH = (\partial H/\partial m)dm$), after simple transformations we obtain the final answer:

$$F_{sing} = \int_m^{m_0} \frac{m\,dm[\chi(m,\tau)]^{-(2\beta+\gamma)/\gamma}[(\beta+\gamma)\varphi(m) - \beta m\varphi'(m)]}{(\beta+\gamma)\varphi(m) - \beta m}. \quad (28)$$

Here, m_0 is the first root of Eq. (17), and $\chi(m, \tau)$ is determined by formula (15). As $m \to m_0$, the susceptibility $\chi(m, \tau)$ behaves like $(m_0 - m)^\gamma$, and the integral formally diverges like

$$\int dm(m_0 - m)^{-2\beta-\gamma-1}.$$

As we pointed out above, this divergence must be removed by analytic continuation of the integral in β and γ from the side $2\beta + \gamma < 0$.

A separate analysis is required for the case $2\beta + \gamma = 2$, which corresponds to a logarithmic specific heat. We take the limit $\alpha = 2 - 2\beta - \gamma \to 0$ in (28). For this, we must first analytically continue the integral in α from the side $\alpha > 2$. This can be done as follows.

We write the integrand in (28) in the form

$$T_c\tau^{2\beta+\gamma}(m_0 - m)^{-2\beta-\gamma-1}[r_0 + r_1(m_0 - m) - {}^1\!/_2 A(m_0 - m)^2 + R(m)].$$

Here R(m) is a function which at $m = m_0$ is analytic and goes to zero together with its two derivatives; r_0, r_1 and A are certain constants. Then, integrating over m, we obtain

$$F_{sing} = T_c\tau^{2-\alpha}\left[f_R(m) + r_0\frac{(m_0-m)^{\alpha-2}}{\alpha-2} + r_1\frac{(m_0-m)^{\alpha-1}}{\alpha-1} - \frac{A}{2}\frac{(m_0-m)^\alpha}{\alpha}\right]$$

Here, $f_R(m)$ is the contribution from the function R(m), which converges and does not have singularities as $\alpha \to 0$, $m \to m_0$. Now making $\alpha \to 0$, we obtain

$$F_{sing} = T_c\tau^2\left[f_R(m) - \frac{r_0}{2(m_0-m)^2} - \frac{r_1}{m_0-m} - \frac{A}{2}\ln\frac{m_0-m}{\tau}\right].$$

The last term arose after expansion of the indeterminate form $[(m_0 - m)^\alpha\tau^{-\alpha} - 1]/\alpha$; the term $T_cA\tau^2/2\alpha$, which is regular in τ, was added before the passage to the limit $\alpha \to 0$:

We shall find the specific heats $c^{\pm}_{H=0}$ above and below the transition point. Above T_c, as $H \to 0$ the parameter $m \to 0$ and we obtain

$$F^+_{sing} = T_c\tau^2\left\{f_R(0) - \frac{r_0}{2m_0^2} - \frac{r_1}{m_0} - \frac{A}{2}\ln\frac{m_0}{\tau}\right\};$$

below T_c, as $H \to 0$ we shall have $m \to m_1$ and

$$F^-_{sing} = T_c\tau^2\left\{f_R(m_1) - \frac{r_0}{2(m_1-m_0)^2} + \frac{r_1}{m_1-m_0} - \frac{A}{2}\ln\frac{m_1-m_0}{-\tau}\right\}.$$

The specific heat $c_H = -T_c^{-1}\partial^2F/\partial\tau^2$ has a logarithmic singularity with the same coefficient A above and below T_c. In addition, there is a jump in the specific heat:

$$\Delta c_H = 2\left\{f_R(0) - f_R(m_1) + \frac{r_0m_1(2m_0-m_1)}{2m_0^2(m_1-m_0)^2} - \frac{r_1m_1}{m_0(m_1-m_0)} + \frac{A}{2}\ln\frac{m_1-m_0}{m_0}\right\}.$$

IV. EQUATION OF STATE IN THE FIRST APPROXIMATION. THE THREE-HALVES LAW

In the first approximation of our phenomenological theory, we retain only two terms in the expansion (12):

$$\varphi(m) = m + \varphi_3m^3. \quad (29)$$

Then a relation for the indices β and γ follows immediately from the general formula (18):

$$\beta + \gamma = {}^3\!/_2. \quad (30)$$

For $\varphi = m + \varphi_3m^3$, the equation of state (13), (15) has the simple form

$$M = \chi^{-\beta/\gamma}m, \quad H = \chi^{-(\beta+\gamma)/\gamma}m(1+\varphi_3m^2),$$
$$\chi = C_+\left(\frac{1+3\varphi_3m^2/2\gamma}{\tau}\right)^\gamma. \quad (31)$$

In order that a spontaneous moment exist at $\tau < 0$, $H = 0$, the coefficient φ_3 must be negative. It can be included conveniently in the definition of m:

$$-\varphi_3m^2 = \Theta^2.$$

The equation of state can be rewritten in a parametric form that is explicitly analytic as $\tau \to 0$:

$$(-\varphi_3)^{1/2}M = r^\beta\Theta, \quad (-\varphi_3)^{1/2}H = r^{\beta+\gamma}\Theta(1-\Theta^2),$$
$$C_+^{-1/\gamma}\tau = r(1-3\Theta^2/2\gamma), \quad \chi = r^{-\gamma}. \quad (32)$$

These equations have the same form as the empirical equations from the work of Schofield et al.[3] In this work, experimental data on critical points and Curie points were analyzed by means of the parametric equation of state

$$M = r^\beta\mu(\Theta), \quad H = r^{\beta+\gamma}h(\Theta), \quad \tau = rt(\Theta).$$

The experimental data are well described by formulas of the type (32) containing the coefficient $b^2 = (\gamma - 2\beta)/\gamma(1-2\beta)$ [3] in place of the coefficient $3/2\gamma$. If our relation (30) is fulfilled, then $b^2 = 3/2\gamma$ and our formulas coincide exactly with the empirical formulas from [3].

We now examine the accuracy with which the relation (30) is fulfilled experimentally. The values of β, γ and $2(\beta + \gamma)/3$ are given in Table I. For the two-dimensional Ising model, the indices are known exactly from the Onsager solution. For the three-dimensional Ising model, the results of high-temperature expansions have been used. For real substances, our knowledge of the indices is poor inasmuch as their values depend on the choice of the equation of state used to analyze the experimental data. This indeterminacy has had the con-

Table I

Parameter	System				
	EuO	EuS	CO_2	3-Ising	2-Ising
β	0.37	0.36	0.35	0.31	1/8
γ	1.40	1.39	1.20	1.25	7/4
$^2/_3(\beta+\gamma)$	1.18	1.18	1.03	1.04	5/4

sequence that the results of different experiments differ from each other by more than the indicated experimental errors, so that one has to choose which experiment to trust. The most reliable values, given in Table I, of the indices for ferromagnets and gases were selected by A. V. Voronel'.

V. REFINEMENT OF THE EQUATION OF STATE. THE SECOND SPONTANEOUS MOMENT

We now make the equation of state more precise, by including the term $\varphi_5 m^5$ in the expansion (12):

$$\varphi(m) = m + \varphi_3 m^3 + \varphi_5 m^5. \quad (33)$$

Then the relations (17)–(19) between the indices β and γ and the function $\varphi(m)$ can be brought to the form

$$\frac{\varphi_5}{\varphi_3^2} = \frac{(\beta+\gamma)(\beta+\gamma-1)(2\beta+2\gamma-3)}{\gamma(4\beta+4\gamma-5)^2}. \quad (34)^*$$

It can be seen that if $\beta + \gamma = {}^3/_2$, then $\varphi_5 = 0$, and if $\beta + \gamma = {}^5/_4$, then $\varphi_3 = 0$, in accordance with formula (18).

We turn now to the equation of state. The integration in (15) is elementary. The result can be written conveniently by introducing in place of m the dimensionless parameter θ, by the formula

$$-\varphi_3 m^2 = \frac{\gamma(4\beta+4\gamma-5)}{\beta+\gamma}\frac{b^2\theta^2}{1+(2\beta+2\gamma-3)b^2\theta^2}. \quad (35)$$

Here, b^2 is a constant, which will be encountered frequently below:

$$b^2 = (\beta+\gamma)/[\gamma - 2\beta(2\beta+2\gamma-3)]. \quad (36)$$

For $\beta + \gamma = {}^3/_2$, the parameter θ coincides with the parameter Θ in (32).

Using the parameter θ, we can write the second-approximation equation of state thus:

$$\tau = r(1-b^2\theta^2), \quad (37)$$

$$M/M_c = r^\beta\theta[1+(2\beta+2\gamma-3)b^2\theta^2]^{(4\beta-\gamma)/(2\beta+2\gamma)}, \quad (38)$$

$$H/H_c = r^{\beta+\gamma}\theta(1-\theta^2+\lambda\theta^4), \quad (39)$$

$$\left(\frac{\partial M}{\partial H}\right)_\tau = \chi = \frac{M_c}{H_c}r^{-\gamma}[1+(2\beta+2\gamma-3)b^2\theta^2]^{-5\gamma/(2\beta+2\gamma)}. \quad (40)$$

The coefficient λ in (39) is connected with the critical indices β and γ by the relation

$$\lambda = \frac{\beta}{\beta+\gamma}(2\beta+2\gamma-3)^2 b^4. \quad (41)$$

The constants H_C and M_C are phenomenological constants related to the constant φ_3 in the expansion (33):

$$\varphi_3 = -H_c^{2\beta/\gamma}M_c^{-(2\beta+2\gamma)/\gamma}\frac{\gamma(4\beta+4\gamma-5)}{(2\beta+2\gamma-2)^2[\gamma-2\beta(2\beta+2\gamma-3)]} \quad (42)$$

In its form, the equation of state is completely universal and depends only on the critical indices β and γ. The first-approximation equation is obtained if we put $\beta + \gamma = {}^3/_2$.

*It is noted in ZhETF Pis Red. 16, 255 (1972) [JETP Lett. 16, 179 (1972)] that a factor 2 was left out of this equation [Transl. note].

We shall give a formula for the free energy corresponding to Eqs. (37)–(40); this is calculated by the method of Sec. IV:

$$F_{sing} = -M_c H_c r^{2\beta+\gamma} f(1-b^2\theta^2).$$

Here f(z) is a function that is analytic at z = 0 and can be expressed in terms of hypergeometric functions F(a, b, c, z):

$$f(z) = \sum_{m=0}^{3} R_m f_m(z)\frac{z^m}{2\beta+\gamma-m}, \quad (44)$$

$$f_m(z) = \frac{(1+\varepsilon)^{3\eta/(5-\eta)}}{2b^2}F\left(\frac{-3\eta}{5-\eta}, m-2\beta-\gamma, m+1-2\beta-\gamma, \frac{\varepsilon z}{1+\varepsilon}\right), \quad (45)$$

where

$$R_0 = 2\beta(1+\varepsilon)^2, \quad R_1 = 14\lambda b^{-4} + 3b^{-2} - 2 + \varepsilon(2b^{-2} - 1 + 3\lambda b^{-4}),$$

$$R_2 = -\varepsilon b^{-2} - \lambda b^{-4}(1-3\varepsilon), \quad R_3 = \lambda b^{-4}(2-\varepsilon); \quad (46)$$

λ and b are given by formulas (41) and (36) and

$$\varepsilon = 2\beta + 2\gamma - 3, \quad \frac{3\eta}{5-\eta} = \frac{4\beta-\gamma}{2\beta+2\gamma}.$$

For comparison with experiment, it is convenient to find the coefficients C_+, C_-, B and D in the laws (6), (5) and (21) for the susceptibility, spontaneous moment and high-field moment, and also the coefficients $A_\pm$ in the specific heat $c_H = -T_c^{-1}(\partial^2 F/\partial\tau^2)_{H=0} = A_\pm|\tau|^{2\beta+\gamma-2}$.

Our results for $C_\pm$, B, D and $A_\pm$ are as follows:

$$C_+ = M_c/H_c, \quad (47)$$

$$C_- = \frac{M_c}{H_c}(b^2\theta_1^2-1)^\gamma(1+\varepsilon b^2\theta_1^2)^{-5\gamma/(2\beta+2\gamma)}, \quad (48)$$

$$B = M_c\theta_1(b^2\theta_1^2-1)^{-\beta}(1+\varepsilon b^2\theta_1^2)^{3\eta/(5-\eta)}, \quad (49)$$

$$D = M_c H_c^{-\beta/(\beta+\gamma)}\left(\frac{\beta+\gamma}{\beta}\right)^{\beta/(\beta+\gamma)} b^{-\gamma/(\beta+\gamma)}(1+\varepsilon)^{3\eta/(5-\eta)}, \quad (50)$$

$$A_+ = \frac{M_c H_c}{T_c}(2\beta+\gamma)(2\beta+\gamma-1)f(1), \quad (51)$$

$$A_- = \frac{M_c H_c}{T_c}(2\beta+\gamma)(2\beta+\gamma-1)(b^2\theta_1^2-1)^{-2\beta-\gamma}f(1-b^2\theta_1^2), \quad (52)$$

where θ_1 is the first (smallest) root of the equation $1 - \theta^2 + \lambda\theta^4 = 0$, i.e.,

$$\theta_1^2 = 2/[1+(1-4\lambda)^{1/2}]. \quad (53)$$

In Table II, the dimensionless ratios C_+/C_-, $C_+^\beta B^\gamma/D^{\beta+\gamma}$ from the formulas (47)–(50) are compared with experiment and with numerical calculations for the Ising models. The "experimental" data shown are taken from [3]. It is necessary to bear in mind that the values of the indices and critical coefficients depend on the equation of state taken to analyze the experiment. Therefore, all that one can say on the basis of Table II is that the equation of state of the linear model and our equation of state lead to numerically close results and agree well with experiment. For a complete comparison with experiment, it is necessary to analyze all the experimental curves using our equation of state and assuming

Table II

Parameter *	System							
	$CrBr_3$	Ni	CO_2	Xe	He	β-brass	3-Ising	2-Ising
β	0.37	0,37	0.35	0.35	0.36	0,30	0.31	$^1/_8$
γ	1.21	1.31	1.26	1.26	1.24	1.24	1.25	$^7/_4$
$2(\beta+\gamma)/3$	1.05	1.11	1.07	1.07	1.06	1.03	1.04	$^5/_4$
$\bar{n}$	2.7	2.5	2.6	2.6	2.7	2.8	2.7	$^{15}/_7$
b^2	1.44	1.63	1.45	1.45	1.46	1.30	1.33	$^6/_5$
λ	0.01	0.07	0.02	0.02	0.02	0.00	0.00	0.05
$(C_+/C_-)_T$	3.8	3.7	4.4	4.4	4.0	5.5	5.3	48
$(C_+/C_-)_t$	3.1±0.9	2.9±1.4	4.4	4.1	3.6	5.5	5.2	37
$(C_+/C_-)_{lm}$	3.8	3.9	4.2	4.2	4.0	5.5	5.3	60
$(C_+^\beta B^\gamma/D^{\beta+\gamma})_T$	1.17	1.21	1.21	1.21	1.17	1.18	1.20	0.93
$(C_+^\beta B^\gamma/D^{\beta+\gamma})_t$	1.16±0.07	1.1±0.1	1.20	1.18	1.15	—	1.20	1.32
$(C_+^\beta B^\gamma/D^{\beta+\gamma})_{lm}$	1.16	1.20	1.18	1.18	1.17	1.18	1.18	1.27

*Here, the subscript t denotes date obtained from formulas (47)–(52), the subscript e denotes experimental data [3] (for the Ising models, the results of high-temperature expansions), and the subscript lm denotes results obtained from the linear model [3].

that the critical indices and the coefficients M_0 and H_0 are arbitrary parameters.

In principle, it is also possible to compare other dimensionless ratios, e.g., A_+/A_-, with experiment. However, the indices β and γ are known with insufficient accuracy for this. The point is that, for the experimental values of the indices given in Table II,

$$\alpha = 2 - 2\beta - \gamma \approx 0.05 \qquad (CrBr_3),$$

$$\frac{3\eta}{5-\eta} = \frac{4\beta-\gamma}{2\beta+2\gamma} \approx 0.08 \qquad (CrBr_3).$$

For such small values of α and η, the function f(z) in (44) is approximately equal to

$$f(z) \approx \frac{1}{4b^2}\left\{R_0\left(1-\frac{3\eta}{5\alpha}z^2\right)+R_1\left(z-\frac{3\eta}{5\alpha}z^2\right)-R_2\frac{z^2}{\alpha}\right\}. \qquad (54)$$

For $CrBr_3$, the coefficients R_0, R_1 and R_2 are of order

$$R_0 \sim 1.0, \quad R_1 \sim 0.23, \quad R_2 \sim -0.11.$$

For the value $z = 1 - b^2\theta_1^2 \sim -0.46$ ($CrBr_3$), which determines the specific heat below T_c, all three terms in (54) are of the same order and f(z) depends essentially on the ratio η/α, which is known only in order of magnitude.

Our formulas can be used to refine the values of η and α, knowing the experimental ratio A_+/A_-.

Finally, we give a formula for the metastable moment $\tilde{M}_0$ predicted by the equation of state (37)–(41):

$$\frac{\tilde{M}_0(\tau)}{M_0(\tau)} = \frac{\theta_2}{\theta_1}\left(\frac{b^2\theta_1^2-1}{b^2\theta_2^2-1}\right)^\beta\left(\frac{1+\varepsilon b^2\theta_2^2}{1+\varepsilon b^2\theta_1^2}\right)^{3\eta/(5-\eta)}. \qquad (55)$$

Here, $M_0(\tau)$ is the ordinary spontaneous moment, and

$$\theta_2^2 = \frac{2}{1-(1-4\lambda)^{1/2}} = \frac{1}{\lambda\theta_1^2}$$

is the second root of the equation $1 - \theta^2 + \lambda\theta^4 = 0$. The ratio $\tilde{M}_0/M_0$ depends fairly strongly on the critical indices and can be large. For example, for nickel, $\tilde{M}_0 \approx 3.5M_0$.

VI. DISCUSSION. THE PROBLEM OF JUSTIFICATION

The phenomenological theory constructed is based on two fundamental assumptions:

1) the scaling hypothesis, from which it follows that the function $\varphi(m)$ must not depend explicitly on temperature,

2) the hypothesis that the function $\varphi(m)$ is analytic in the critical region, which means that the series $\varphi(m) = m + \Sigma\varphi_n m^n$ converges sufficiently rapidly.

The scaling hypothesis seems to the author to be sufficiently well-founded. Apart from physical reasoning,[1] there are microscopic justifications[4,5] by field-theory methods. The microscopic justifications cannot be considered rigorous, since they operate with divergent series of Feyman diagrams. In particular, it is difficult to understand in the framework of the microscopic approach how the critical indices β and γ could be other than universal, i.e., depend not only on the symmetry, but also on the parameters of the system. This question has been analyzed in part in the author's paper,[6] in which a field-theory model with interaction gM^6 is analyzed. In the practically attainable subcritical region of distances $\ln(r/r_0) \sim 1$, the effective indices at the transition point depend on the non-universal constant g.

The analyticity hypothesis corresponds to our physical ideas on critical phenomena and, as was shown above, works well in practice. However, from a theoretical point of view, this is insufficient, and it would be desirable to know the analytic properties of $\varphi(m)$, if only in some model.

For the Ising model, the Lee-Yang analysis[2] (cf. also [1]) shows that the only singularities of the equation of state are branch points at

$$H = \pm\,\text{const}\cdot i\tau^{\beta+\gamma}.$$

These branch points determine the radius of convergence of the usual series in powers of $H\tau^{-\beta-\gamma}$. We shall see what these branch points mean for our function $\varphi(m)$. If we retain the first terms, $\varphi(m) = m + \varphi_3 m^3$, then, as $m \to \pm i\infty$, as is easily seen from our formulas, the magnetic field actually tends to an imaginary value, and the susceptibility goes to infinity close to this point. In other words, one can obtain singularities of the Lee-Yang type by assuming $\varphi(m)$ to be simply a polynomial.

It is important, however, that the susceptibility goes to infinity near these singularities. This property is also conserved in the more general case when $\varphi(m)$ is not a polynomial, but an entire function going to infinity as $m \to \pm i\infty$. Indeed, making $m \to \pm i\infty$ in (15), we obtain

$$\chi(m,\tau)\to\tau^{-\gamma}\exp\left(\frac{\gamma}{\beta+\gamma}\ln\left|\frac{\varphi(m)}{\mathrm{const}}\right|\right). \tag{56}$$

If we now substitute (56) in the formula (13) for H, then $\varphi(m)$ in (13) cancels and

$$H\to\mathrm{const}\cdot\tau^{\beta+\gamma}\frac{\varphi(m)}{|\varphi(m)|}.$$

For $m \to \pm i\infty$, the function $\varphi(m) = \pm i\,|\varphi(m)|$, so that these are singularities of the Lee-Yang type. Thus, assuming $\varphi(m)$ to be an entire function, we can obtain those of the Lee-Yang singularities near which the susceptibility goes to infinity, i.e., the density of zeros of the partition function goes to zero no more rapidly than linearly. For the Lee-Yang singularity closest to the coordinate origin H = 0, this property is fulfilled—the density of zeros obeys a scaling law with exponent $1-\gamma < 1$. If $\chi \to \infty$ for the other singularities also, or if the latter are situated outside the critical region $|H| \propto |\tau|^{\beta+\gamma} \to 0$, then $\varphi(m)$ will be an entire function.

We shall discuss one more question, which is very important for our theory. We have expressed all observable quantities in the critical region in terms of the entire function $\varphi(m)$, the Taylor coefficients of which we have assumed to be phenomenological parameters. Might it not be possible, however, to measure the function $\varphi(m)$ directly in experiments?

From a geometric point of view, $\varphi(m)$ is the isocline of a family of isotherms, i.e., the curve along which the derivative $\chi = (\partial M/\partial H)_T$ is constant. If it were found possible to do an experiment in which the dependence of the magnetization on the magnetic field at constant susceptibility, and not at constant temperature, was measured, then this would be very important. Since the susceptibility is very large in the critical region, to hold it constant is, at first sight, not difficult. In doing this, there is no necessity to measure and control the temperature if a method can be found for controlling the susceptibility directly. If the scaling hypothesis is correct, all the points must lie on one smooth curve $\varphi(m)$. After this, it will be possible to find all the thermodynamic quantities and critical indices with great accuracy from our formulas.

CONCLUSION

This paper proposes a quantitative approach to the thermodynamics of second-order phase transitions; this is a development and generalization of Landau's original idea of expanding the equation of state in powers of the order parameter. In the framework of the scaling hypothesis with arbitrary critical indices, it is possible, nevertheless, to generalize the concept of the order parameter and the external field corresponding to it in such a way that for these quantities m and h, unlike the usual M and H, the equation of state is universal and is defined by a rapidly convergent series. The first two terms of the series are found to be sufficient to describe all the experimental data, to within a few per cent accuracy, by means of only two phenomenological parameters —the critical indices β and γ.

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[1]A. Z. Patashinskii and V. L. Pokrovskiĭ, Zh. Eksp. Teor. Fiz. **50**, 439 (1966) [Sov. Phys.-JETP **23**, 292 (1966)].
[2]T. D. Lee and C. N. Yang, Phys. Rev. **87**, 410 (1952).
[3]P. Schofield, J. D. Litster, and J. T. Ho, Phys. Rev. Lett. **23**, 1098 (1969).
[4]A. M. Polyakov, Zh. Eksp. Teor. Fiz. **55**, 1026 (1968) [Sov. Phys.-JETP **28**, 533 (1969)].
[5]A. A. Migdal, Zh. Eksp. Teor. Fiz. **55**, 1964 (1968) [Sov. Phys.-JETP **28**, 1036 (1969)].
[6]A. A. Migdal, Zh. Eksp. Teor. Fiz. **59**, 1015 (1970) [Sov. Phys.-JETP **32**, 552 (1971)].

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