

SCALING THEORY AND THE CLASSIFICATION OF PHASE TRANSITIONS

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The recent classification theory for phase transitions (R. Hilfer, *Physica Scripta* **44**, 321 (1991)) and its relation with the foundations of statistical physics is reviewed. First it is outlined how Ehrenfests classification scheme can be generalized into a general thermodynamic classification theory for phase transitions. The classification theory implies scaling and multiscaling thereby eliminating the need to postulate the scaling hypothesis as a fourth law of thermodynamics. The new classification has also led to the discovery and distinction of nonequilibrium transitions within equilibrium statistical physics. Nonequilibrium phase transitions are distinguished from equilibrium transitions by orders less than unity and by the fact that equilibrium thermodynamics and statistical mechanics become inapplicable at the critical point. The latter fact requires a change in the Gibbs assumption underlying the canonical and grandcanonical ensembles in order to recover the thermodynamic description in the critical limit.

1. Introduction

According to current theories of critical phenomena, the twin concepts of scaling and universality play a central role for the physics of phase transitions.¹⁻³ The twin concepts are however not equally universal. In fact it is becoming increasingly apparent that scaling is a far more general concept than universality.³ While scaling applies very fruitfully to almost all systems with many degrees of freedom even outside theories of critical phenomena the same is not true for the universality concept. Both concepts arise simultaneously within the renormalization method for the solution of models in statistical mechanics. Given their closely related origin, the question, why the scaling concept is so much more general than the universality concept, becomes important.

More important than the relation between scaling and universality is the connection between scaling and classical thermodynamics. Classical thermodynamics is a general theory of many-body phenomena which derives its generality from the general validity and simplicity of its hypotheses. How can thermodynamics fail to reproduce the most general and ubiquitous features of continuous phase transitions? Why is it necessary to attach the scaling hypothesis as a "fourth law" to

thermodynamics? Is the generality of scaling laws related to the general validity of the laws of thermodynamics? These fundamental questions remain unanswered by current theories of statistical physics.

Despite of its fundamental importance and much initial interest,⁴ the question whether scaling can be obtained within thermodynamics was put to rest after the theory of renormalization allowed to derive scaling within statistical mechanics. Recently⁵⁻⁸ the discussion about thermodynamic theories of phase transitions was reopened and the objective of the present paper is to give a brief review over some recent results.

Given the fact that thermodynamics is not concerned with the microscopic origin of its potentials it is clear that a thermodynamic theory of phase transitions can at best provide a mathematical characterization of singularities in thermodynamic potentials along the lines of Ehrenfest⁹ or discuss restrictions arising from the basic laws. A thermodynamic theory cannot provide numerical values for critical point exponents or explicit solutions for scaling functions. Nevertheless thermodynamics can provide useful general information on phase transitions. This was demonstrated by Milton and Fisher⁵ who classified anomalous first order transitions arising in systems with many-body interactions of indefinitely high order. The present paper will review more recent results⁶⁻⁸ obtained by generalizing the classification theory of Ehrenfest.⁹

2. Classification of Phase Transitions

Let me begin by recalling that Ehrenfest⁹ defined a p th order transition as one in which the j th order derivatives of a thermodynamic potential with $j \leq p - 1$ are continuous while the p th derivative shows a jump discontinuity. To be more specific consider a magnetic system whose free energy $F(t, h)$ is written as a function of reduced temperature $t = (T - T_c)/T_c$ and the ordering field h . The origin ($t = 0, h = 0$) is assumed to belong to a critical manifold, and represents the critical point of interest. Let $\mathcal{C} : \mathbb{R} \rightarrow \mathbb{R}^2, s \mapsto (t(s), h(s))$ be an arbitrary smooth curve through the critical point such that $t(0) = 0$ and $h(0) = 0$. The phase transition can now be classified by applying Ehrenfests idea to the singular part of the free energy restricted to the curve \mathcal{C} . Define the limits

$$A^\pm(\mathcal{C}) = \lim_{s \rightarrow 0^\pm} \frac{d^p F_{\text{sing}}(t(s), h(s))}{ds^p}. \quad (2.1)$$

for the p th derivative of the singular part of the free energy restricted to the curve \mathcal{C} . The order of the phase transition along the curve \mathcal{C} was defined by Ehrenfest as the smallest integer $p(\mathcal{C}) \geq 1$ such that $A^+(\mathcal{C}) \neq A^-(\mathcal{C})$. Many authors have discussed the inadequacy of Ehrenfests classification.^{5,10,11,12} As a consequence, it has become customary to distinguish only between first order and continuous transitions. Recently, however, it was found in Refs. 6 and 7 that Ehrenfests classification remains generally adequate and that analytic continuation in p yields a precise classification of continuous transitions according to their order.

The key step of Ref. 6 towards a quantitative distinction between continuous phase transitions of different order was to rewrite (2.1) in terms of a finite difference quotient. Rewriting (2.1) for the singular part of the free energy reads then

$$A^\pm(\mathcal{C}) = \lim_{s \rightarrow 0^\pm} \lim_{N \rightarrow \infty} \left(\frac{|s|}{N} \right)^{-p} \sum_{j=0}^{N-1} (-1)^j \binom{p}{j} F \left(t \left(s \mp \frac{js}{N} \right), h \left(s \mp \frac{js}{N} \right) \right) \quad (2.2)$$

where p is an arbitrary integer variable and the subscript of F has been suppressed to shorten notation. This reformulation of Eq. (2.1) can be analytically continued in p to give

$$A^\pm(\mathcal{C}) = \lim_{s \rightarrow 0^\pm} \lim_{N \rightarrow \infty} \Gamma(-p)^{-1} \left(\frac{|s|}{N} \right)^{-p} \sum_{j=0}^{N-1} \frac{\Gamma(j-p)}{\Gamma(j+1)} F \left(t \left(s \mp \frac{js}{N} \right), h \left(s \mp \frac{js}{N} \right) \right), \quad (2.3)$$

where now $p \in \mathbb{R}$. Using the analyticity away from the critical point it was further shown in Ref. 7 that

$$A^\pm(\mathcal{C}) = \lim_{s \rightarrow 0^\pm} \Gamma(-p)^{-1} |s|^{-p} \sum_{k=0}^{\infty} \frac{(\mp s)^k}{(k-p)k!} \frac{d^k F(t(s), h(s))}{ds^k}. \quad (2.4)$$

It follows that there exists a unique pair of numbers $p^\pm(\mathcal{C})$ such that $A^\pm(\mathcal{C}) = 0$ for $p < p^\pm(\mathcal{C})$ and $A^\pm(\mathcal{C}) = \infty$ for $p > p^\pm(\mathcal{C})$. The dependence on the particular curve has been indicated explicitly. This suggests the definition

$$p^\pm(\mathcal{C}) = \sup\{p \in \mathbb{R} | p \geq 1, A^\pm(\mathcal{C}) < \infty\} \quad (2.5)$$

for the *generalized order* of the phase transition along the curve \mathcal{C} . The difference $\Delta A = |A^+ - A^-|$ can be used to characterize the *strength* of the transition. For the Ising transition along the temperature direction, one has $p^+ = p^- = 2 - \alpha$ where α is the specific heat exponent. Similarly the order along the critical isotherm ($t = 0$) is found to be $1 + 1/\delta$ by exchanging the role of t and h . Depending on the nature of the critical point the order may or may not be path dependent. The former occurs near a multicritical point.

3. Scaling in Thermodynamics

Analytic continuation of Ehrenfests thermodynamic theory leads directly to power laws with nonclassical exponents as demonstrated in the previous section. In addition thermodynamic multiscaling arises because both amplitudes and exponents are in general path dependent.^{6,7} Equation (2.4) shows that the singular path of the free energy has the form

$$F(t(s), h(s)) = Y(\mathcal{C}) |s|^{p(\mathcal{C})}, \quad (3.1)$$

where Y and p are functions of the parameters defining the curve \mathcal{C} . Equation (3.1) represents a very general form of power law scaling. It includes general forms of multiscaling defined as a scaling form for which the critical indices may become scale dependent¹³⁻¹⁷

The last statement is readily verified by expanding the curve \mathcal{C} around $s = 0$. Consistency with Eq. (3.1) suggests to require that \mathcal{C} can be expanded into a Frobenius series having the general form $|t(s)| = t_0|s|^{\lambda_t} + \mathcal{O}(|s|^{\lambda_t+1})$ and $|h(s)| = h_0|s|^{\lambda_h} + \mathcal{O}(|s|^{\lambda_h+1})$. Obviously, in the limit $s \rightarrow 0$, only the first term depending on the parameters t_0 , h_0 , λ_t and λ_h remains important. To obtain the behaviour of F in the t -direction near the critical point, one solves $|t(s)|$ and inserts the result into (3.1) and into $|h(s)|$. This gives $|h| = a|t|^\Delta$ near the critical point with $a = h_0 t_0^{-\Delta}$ and $\Delta = \frac{(\lambda_h)}{\lambda_t}$. Thus the free energy obeys the generalized scaling law

$$F(t, h) = Z(a, \Delta)|t|^{q(a, \Delta)}, \quad (3.2)$$

where $q(x, y)$ and $Z(x, y)$ are arbitrary functions. From Eq. (3.2) arise two natural forms of multiscaling if either one of the parameters a or Δ is expressed as a function of t and h . In the first case the scaling variable is $a = |h|/|t|^\Delta$, in the second case $\Delta = \log(|h|/a)/\log|t|$. While the first scaling variable has been used traditionally the second has only recently appeared in the multiscaling context.¹³⁻¹⁷

4. Transitions of Order Less Than Unity

The previous sections have established that thermodynamics provides a general classification of phase transitions according to their order p and that this classification theory implies scaling, or more generally multiscaling. It is then natural to ask to what extent are the values $p \in \mathbb{R}$ for the order restricted by the laws of thermodynamics. In particular, are transitions with order $p < 1$ thermodynamically admissible or not? This question was investigated in Ref. 8 and a selection of the results of that study will be discussed next.

In classical thermodynamics the energy function $U(S, V)$ must be a convex, monotonically increasing and almost everywhere differentiable function of the coordinates S , entropy, and V , volume.^{18,19} Classically the state variables satisfy $0 \leq V < \infty$, $-\infty < S < \infty$, and $-\infty < U < \infty$, while for quantum systems S and U must also be bounded from below. These conditions are both necessary and sufficient for thermodynamic stability. It is usually also required that $U(S, V)$ be single-valued but this is a less stringent requirement. Gibbs was willing to consider multivaluedness in his theory of metastable states.

Consider a thermodynamic system described by the potential $U(S, V)$. The classification of a transition at a critical point (S_c, V_c) is achieved by classifying the transition along all possible thermodynamic processes crossing the critical point. Let me for simplicity restrict the discussion to an isochore. If the transition at S_c is of order p , with $p = p^+ = p^-$, then it follows from (2.1) and (2.5) that $U(S)$ has the form

$$U(S) = U_r(S) + U^\pm(S)|S - S_c|^p, \quad (4.1)$$

where $U_r(S)$ is the regular part and the critical amplitudes A^\pm are given as

$$\lim_{S \rightarrow S_c^\pm} U^\pm(S) = A^\pm. \quad (4.2)$$

Consequently any phase transition with $S_c < \infty$ and order $p < 1$ violates convexity for U or the condition $U < \infty$, and is thus forbidden by the laws of thermodynamics. This appears to restrict thermodynamically admissible transitions to the range $p \geq 1$.

But the laws of thermodynamics do not require $S_c < \infty$. To show this consider an energy function of the form

$$U(S) = MS + \tilde{U}(S)S^{-p} \quad (4.3)$$

where $p > 0$ and $0 \leq M < \infty$ is a finite constant. $\tilde{U}(S)$ is a single valued, monotonically increasing, convex and almost everywhere differentiable function which is assumed to have a Laurent-expansion of the form

$$\tilde{U}(S) = U_\infty + \sum_{k=1}^{\infty} U_k S^{-k} \quad (4.4a)$$

and is assumed to be such that

$$\lim_{S \rightarrow 0} \tilde{U}(S)S^{-p} = U_0. \quad (4.4b)$$

The proposed $U(S)$ is compatible with all the laws of thermodynamics and has a phase transition of order $p > 0$ at infinite entropy. Note that the range $0 < p < 1$ is now admissible while for $S_c < \infty$ it was not.

The energy function $U(S)$ given in (4.3) implies that the system is restricted to a finite temperature range $0 < T < T_c$ where $T_c = M$. This result appears to establish a contradiction between thermodynamics and equilibrium statistical mechanics because the conventional canonical partition sum is defined for *all* values of $\beta = 1/k_B T$ where k_B denotes Boltzmann's constant. I shall return to this problem after exploring the consequences for the thermodynamic free energy. To explore thermodynamics first, and statistical mechanics second is the correct methodological order of investigation, because statistical mechanics must conform to thermodynamics and not *vice versa*.

The singular behaviour of the free energy $F(T)$ corresponding to the function $U(S)$ as given by Eqs. (4.3) and (4.4) is obtained through a Legendre transformation as

$$\lim_{T \rightarrow T_c} \frac{F(T)}{(T_c - T)^{\frac{p}{p+1}}} = \frac{(1+p)U_\infty}{(pU_\infty)^{\frac{p}{p+1}}} \quad (4.5)$$

where as before $T_c = M$. The free energy shows a finite temperature phase transition of order $(p/p+1) < 1$ for all $p > 0$ as T_c is approached from below.

The foregoing considerations raise the question as to what happens if the system is heated from a temperature $T_1 < T_c = M$ to a temperature $T_2 > T_c = M$ by placing it into an appropriate heat bath. If thermodynamics is applicable in the vicinity of both temperatures it must be concluded that the transition from T_1 to T_2 (or backwards) can never be achieved as a quasistatic process. The system cannot exist in equilibrium at $T = T_c$ and it therefore drops out of equilibrium upon heating from below T_c as well as upon cooling from above T_c . Therefore a phase transition of order $p^- < 1$ requires an accompanying transition of order $0 \leq p^+ < 1$ when approaching T_c from above.

From this follows immediately that $S(T) \rightarrow \mp\infty$ as $T \rightarrow T_c^\pm$. Thus transitions with $p < 1$ are *fundamentally asymmetric*. Moreover the third law requires existence of a second "critical" temperature $T_0 > T_c$ defined by the condition

$$S(T_0) = 0. \quad (4.6)$$

Consequently the system cannot be described by thermodynamics (including the third law) in the whole range $T_c < T < T_0$. The transition is *fundamentally broadened* by quantum effects. The fact that $F(T)$ is now only locally but not globally concave implies that $U(S)$ becomes multivalued. This does not violate the second law because there exists no quasistatic connection between different globally convex sheets. The critical temperature T_c can never be reached through a quasistatic thermodynamic process, neither from above nor from below, and it resembles absolute zero in this respect.

In addition to predicting a temperature range $T_c < T < T_0$ in which the system cannot exist in equilibrium, thermodynamics predicts two more temperatures T_\pm defining the critical region. They are the solutions of the tangent equations

$$S_+(T_+) = S_-(T_-) = \frac{F_-(T_-) - F_+(T_+)}{T_- - T_+}. \quad (4.7)$$

An equation analogous to (4.7) may be derived also for transitions with $p > 1$ by considering higher derivatives. Equation (4.7) or its analogues may be used as a precise definition of the "critical region". For transitions with $p < 1$ there exist four characteristic temperatures which generally obey the inequalities $T_- < T_c < T_0 < T_+$ while for transitions with $p > 1$ the temperature T_0 is absent.

Summarizing the preceding discussion, thermodynamics allows phase transitions of order $p < 1$ if the potential $U(S, V)$ is allowed to become multi-valued. Transitions with $p < 1$ are fundamentally broadened and they are asymmetric. This immediately brings to mind nonequilibrium phenomena as a realm for possible realizations and it was indeed found in Ref. 8 that the entire phenomenology of the glass transition may be derived from the assumption that there exists a transition with $p < 1$ underlying the glass transition. But a discussion of those results would go beyond the scope of this brief review. Transitions of order $p < 1$ will be

called *non-equilibrium phase transitions* to distinguish them verbally from *equilibrium phase transitions* having $p > 1$. Note that first order transitions are marginal, and are therefore not covered by this distinction.

5. Consequences for Statistical Mechanics

Nonequilibrium transitions in the sense defined above present a serious problem to statistical mechanics. The canonical free energy $F_{\text{can}}(T, V)$ is a well defined convex function of β over the whole temperature range $0 < \beta < \infty$. Correspondingly $U_{\text{can}}(S, V)$ must be single valued. The convexity of F holds already before passing to the thermodynamic limit.¹⁸ This raises the problem how convexity can ever be violated in statistical mechanics, before or after taking the limit? Is there a mathematical mechanism similar to the classification scheme in thermodynamics through which statistical mechanics could become inapplicable at a critical point?

The answer was found to be positive in Ref. 8. The mechanism in question is the same breakdown of the central limit theorem in the *critical limit* that is familiar from equilibrium transitions.²⁰ To define the critical limit consider a regularized system with Hamiltonian $\mathcal{H}\{\psi\}$ on a d -dimensional hypercubic lattice of volume $V = L^d$ and lattice spacing a . If L is the linear dimension of the system then $(L/a)^d$ is the number of lattice points. Let the system be at a noncritical temperature T such that its correlation length ξ for energy fluctuations is finite. More generally ξ is the correlation length corresponding to those fluctuations which become critical. Divide the system into blocks of size ξ . Then there are $N = (L/\xi)^d$ blocks each of which contains $M = (\xi/a)^d$ degrees of freedom. The *critical limit* is defined as the limit in which

$$a \rightarrow 0, L \rightarrow \infty, T \rightarrow T_c \text{ such that } aL = \xi. \quad (5.1)$$

In this limit the number of uncorrelated blocks grows as $N = a^{-d}$ and the number of degrees of freedom inside each block grows simultaneously as $L^d = V$. The correlation length ξ diverges in units of a . The critical limit combines three limits: 1. the thermodynamic limit controlling the number of degrees of freedom in each block; 2. the continuum limit controlling the number of uncorrelated blocks and 3. the approach to the critical point.

Let $\psi_{i,N}(j)$ denote a physical observable ψ at lattice site j ($j = 1, \dots, M$) inside the block i ($i = 1, \dots, N$). The lattice sites inside each of the N blocks are labeled from 1 through M . The probability distribution $e^{-\beta\mathcal{H}\{\psi\}}$ induces a probability distribution on the ψ variables and therefore the sums

$$\psi_N = \sum_{i=1}^N \psi_{i,N} = \sum_{i=1}^N \sum_{j=1}^M \psi_{i,N}(j) \quad (5.2)$$

are in general random variables. The $\psi_{i,N}$ are called *block variables*. Note that the block variables are uncorrelated by construction while the site variables $\psi_{i,N}(j)$ are strongly correlated in the critical limit.

The *ensemble interpretation* of statistical mechanics requires that the block variables become statistically independent and identically distributed in the critical limit. The first equality of Eq. (5.2) implies that the distribution of the random variable ψ_N becomes infinitely divisible in the critical limit.²¹ The usual assumption of the real space renormalization group is even stronger. It demands that in the critical limit the distribution of ψ_N is identical to the distribution of the individual block variables $\psi_{i,N}$ except for location and scale parameters. The shorthand notation $X \stackrel{d}{=} cY + b$ will be used to indicate that the distributions of the random variables X and Y differ only by location and scale parameters. If the renormalization assumption is made then the question arises whether there exist constants $c_N > 0$ and $b_N \in \mathbb{R}$ such that

$$\psi_N \stackrel{d}{=} c_N \psi_{i,N} + b_N \quad (5.3)$$

holds in the critical limit. This question has been studied in probability theory.²¹ If Eq. (5.3) holds then the distribution of ψ_N is stable and the norming constants have the form $c_N \equiv N^\nu$ with $1/2 \leq \nu < \infty$. The central limit theorem corresponds to the case $\nu = 1/2$ where fluctuations become Gaussian. The value $\nu = 1$ is special in several respects. For $\nu > 1$ not only correlations but also averages diverge.

The exponent ν is determined by the Hamiltonian and it classifies possible critical behaviour in statistical mechanics. Transitions with $1/2 \leq \nu < 1$ correspond to equilibrium transitions with diverging correlations but finite expectation values. Transitions with $\nu > 1$ correspond to nonequilibrium transitions with diverging expectation values. The exponent ν is analogous to the thermodynamic order p and must be related to it. If ξ is the thermal correlation length and ψ the energy then ν is identified as the usual correlation length exponent. The relation with p is then given by the hyperscaling relation

$$p = d\nu \quad (5.4)$$

which holds for $\nu \neq 1$, $\nu \neq 1/2$. Remember that $p = 2 - \alpha$ where α is the specific heat exponent. The cases $\nu = 1/2$, $\nu = 1$ (and also $\nu = \infty$) must be excluded because in these cases the possible limiting distributions in (5.3) are not sufficiently characterized by their values of ν . It is important to note that Eq. (5.4) holds only if the source of fluctuations is unique, resulting, for instance, from thermal motion. In the presence of more than one source for fluctuations, e.g., in spin glasses having quenched disorder, Eq. (5.4) need not hold.

The next question is how the conventional formulation of statistical mechanics must be modified in order to be able to reproduce the divergence of thermal expectation values when $\nu > 1$. The answer depends on the choice of ensemble. The microcanonical formulation of statistical mechanics remains unchanged. If a microscopic Hamiltonian gives rise to a $p < 1$ transition then qualitatively new physics enters at the transition and it is necessary to reconsider the definition of

the microscopic degrees of freedom. This necessity does not affect the microcanonical formalism although it may require to switch to the microscopic Hamiltonian. An example is the glass transition. Although it is possible to describe the glass at low temperature as a slow liquid it is better to describe it as a solid with quenched disorder. The nonuniqueness of the microscopic description implies multivaluedness of the microcanonical density of states and hence multivalued thermodynamic potentials in agreement with the previous section.

For the canonical and grandcanonical formulations of statistical mechanics the situation is different, because temperature appears explicitly in the basic probability densities. If the Hamiltonian gives rise to a nonequilibrium critical point then care must be taken to associate thermodynamic derivatives of the partition function, such as temperature, with the correct sheet of $U(S, V)$. This can be accomplished through a renormalization of temperature. Therefore the basic assumption of statistical mechanics in the canonical and grand canonical formulation must be modified. The canonical ensemble is redefined as

$$\rho_{\text{can}} = \frac{\exp[-\beta\mathcal{H}]}{Z_{\text{can}}}; \quad (5.5a)$$

$$Z_{\text{can}} = \text{Tr}\{\exp[-\beta\mathcal{H}]\}; \quad (5.5b)$$

$$F_{\text{can}}(T, V, N) = -(\beta)^{-1} \ln Z_{\text{can}}(T, V, N); \quad (5.5c)$$

$$\beta = \frac{1}{k_B(T - T_c)}, \quad (5.6)$$

where T_c is defined as the critical point with $\nu > 1$ which is closest to the temperature $T > T_c$ at which averages are to be calculated. This definition is unique if absolute zero, $T = 0$, is also interpreted as a nonequilibrium critical point. In (5.5) V is the volume, N the number of particles and k_B the Boltzmann constant as usual. Equation (5.6) was called *temperature renormalization* in Ref. 8. Similarly, if calculating in the grand canonical ensemble the parameter $\beta\mu$ must be replaced by

$$\beta\mu = \frac{\mu}{k_B(T - T_c)}. \quad (5.7)$$

Apart from this renormalization of temperature all calculations of statistical averages can be performed in exactly the same way as when $T_c = 0$ by replacing β with β . This will ensure the correct correspondence with thermodynamics including the special role played by temperature. Equations (5.5) through (5.7) emphasize and elucidate a basic difference for calculations just above a nonequilibrium transition. The value of T_c is not known *a priori*. In general calculations require T_c as experimental input. Note that in the limit $T_c \rightarrow 0$, Eq. (5.5) reduces to the traditional form of the basic assumption.

Equation (5.5) applies also for $p > 1$ equilibrium transitions, and a similar need for *a priori* information occurs in that case as the problem of critical dimensions. In order to perform an ϵ -expansion for critical exponents one needs to know the upper critical dimension. If the upper critical dimension is defined as the dimension

beyond which the theory becomes Gaussian, i.e., $\nu = 1/2$, then from equation (5.4) follows $d_u^e = 2p$. But the order p of the transition is not known before calculating the exponents and thus the upper critical dimension is not known *a priori*. The same applies to the lower critical dimension defined as the dimension at which the theory becomes Cauchyian, i.e., where $\nu = 1$. To say that the Landau-Ginzburg-Wilson theory has $d_u^e = 4$ and $d_l^e = 2$ is then equivalent to the assertion $1 \leq p \leq 2$. The Onsager solution has $\nu = 1$ and $p = 2$ and therefore the solved model must have $d = 2$. No conclusions may be drawn from this for the Ising model in any other dimension, larger or smaller.

The concept of critical dimensions is useful in cases where experimental or numerical information on ν or α is known. Suppose it is known that $p_l \leq p \leq p_u$ and $\nu_l \leq \nu \leq \nu_u$. It then follows that the dimensionality of the system must fall within the range $(p_l/\nu_u) \leq d \leq (p_u/\nu_l)$. This works well for equilibrium transitions. Suppose that one is confronted with an experimental determination of $\nu = 0.65 \pm 0.05$ and wishes to test the idea that the transition is 3d-Ising like where $p_{\text{Ising}} = 1.89 \pm 0.02$. Then the system should fall into the range $2.6 \leq d \leq 3.2$.

The discussions in this and the previous sections have shown that statistical mechanics as well as thermodynamics both contain within themselves a mathematical mechanism which limits their own applicability. In traditional thermodynamics the mathematical classification scheme reviewed in Sec. 2 implies that $U(S, V)$ may become multivalued. In statistical mechanics the limit theorems of probability theory require to modify the temperature ensembles by renormalizing β as in (5.6). The physical phenomena corresponding to these mathematical mechanisms are diverging entropies in thermodynamics and diverging expectation values in statistical mechanics. The appearance of singularities with $p < 1$ has been termed *spontaneous ergodicity breaking*⁸ in analogy to *spontaneous symmetry breaking* for $p > 1$ transitions. In a nonequilibrium transition not only the symmetry of the Hamiltonian is broken but the Hamiltonian itself breaks down and the microscopic degrees of freedom must be redefined. Nonequilibrium transitions do not have order parameters in the traditional sense because there exists no continuity across the critical point.

6. Conclusion

Thermodynamics allows to classify every phase transition according to its order $p \geq 0$. Transitions with order $p > 1$ are well known as continuous phase transitions in the theory of equilibrium critical phenomena. Transitions with order $p < 1$ are a novel class of transitions. Although they are allowed by the laws of thermodynamics, they correspond to nonequilibrium phase transitions in the sense that equilibrium theories become inapplicable at the critical point. First order transitions are marginal. The classification theory gives rise to a very general form of multiscaling from which traditional scaling emerges as a special case. This eliminates the need to postulate scaling as a fourth law in the context of thermodynamics.

The discovery of phase transitions with order $p < 1$ necessitates to reconsider the connection between statistical mechanics and thermodynamics. Statistical mechanics is shown to contain an analogous classification scheme for phase transitions. Each phase transition in statistical mechanics is characterized by the index ν of a stable distribution governing the critical limit. Equilibrium transitions are characterized by $1/2 \leq \nu < 1$, nonequilibrium transitions by $\nu > 1$. Transitions with $\nu = 1$ are again marginal. The classification schemes of thermodynamics and statistical mechanics are related through the hyperscaling relation (5.4). The requirement that calculations in statistical mechanics should reproduce the thermodynamic behaviour of the appropriate sheet of multivalued thermodynamic potentials requires to modify the formulation of the canonical and grandcanonical ensembles. For calculations above a nonequilibrium critical point, the temperature must be renormalized according to (5.6). The discovery of nonequilibrium transitions and the predicted temperature renormalization are in perfect agreement with experiment.⁸

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