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CLASSIFICATION THEORY FOR PHASE TRANSITIONS

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A refined classification theory for phase transitions in thermodynamics and statistical mechanics in terms of their orders is introduced and analyzed. The refined thermodynamic classification is based on two independent generalizations of Ehrenfests traditional classification scheme. The statistical mechanical classification theory is based on generalized limit theorems for sums of random variables from probability theory and the newly defined block ensemble limit. The block ensemble limit combines thermodynamic and scaling limits and is similar to the finite size scaling limit. The statistical classification scheme allows for the first time a derivation of finite size scaling without renormalization group methods. The classification distinguishes two fundamentally different types of phase transitions. Phase transitions of order $\lambda > 1$ correspond to well known equilibrium phase transitions, while phase transitions with order $\lambda < 1$ represent a new class of transitions termed anequilibrium transitions. The generalized order λ varies inversely with the strength of fluctuations. First order and second order transitions play a special role in both classification schemes. First order transitions represent a limiting case separating equilibrium and anequilibrium transitions. The special role or second order transitions is shown to be related to the breakdown of hyperscaling. For anequilibrium transitions the nature of the heat bath in the canonical ensemble becomes important.

1. Introduction

A number of recent publications[1–5] has reopened the discussion concerning the classification of critical behaviour. In Ref. 1 a thermodynamic classification of normal and anomalous first order phase transitions was given. In Refs. 3 and 4 it was shown that continuous phase transitions can also be usefully classified by extending the thermodynamic classification scheme of Ehrenfest. Based on the generalized classification scheme, a new class of phase transitions having order less than unity was discovered[5] and it was shown that the novel transition type is allowed by the laws of classical thermodynamics. The identification of the corresponding statistical mechanical classification theory however remained incomplete.

My objective in this paper is to elucidate the equivalence between the statistical mechanical and the thermodynamical classification theories in more detail. To this end the thermodynamic classification scheme introduced in Refs. 3

and 4 will first be refined. Phase transitions of order less than unity which were introduced in Ref. 5 will be discussed thermodynamically without introducing multivalued thermodynamic potentials. Then the statistical mechanical classification will be shown to arise from the concept of finite ensemble scaling which is closely related to finite size scaling theory. The statistical classification theory gives rise to a new universal mechanism for the breakdown of hyperscaling which differs from the traditional mechanism of dangerous irrelevant variables.[6]

Discontinuities and divergences of thermodynamic potentials along curves which cross a critical manifold can be characterized mathematically through their generalized orders $\lambda \geq 1$ (with $\lambda \in \mathbb{R}$) as well as their strengths.[3,4] Besides providing a convenient language the classification scheme implies multiscaling for thermodynamic phase transitions.[3,4] Multiscaling has been defined as a scaling form in which the critical exponents are functions of the scaling variables.[7] The simplest form of multiscaling occurs at a multicritical point but recently more interesting cases have been discussed.[8–16] The derivation of multiscaling from analytic continuation of the Ehrenfest scheme represents a derivation of thermodynamic scaling results without the use of renormalization group ideas.

Given these results it is natural to ask whether phase transitions of order $\lambda < 1$ are thermodynamically admissible or not. A rash answer would be negative because such transitions appear to violate thermodynamic stability requirements. A more cautious response however is useful.[5] Transitions having order $\lambda < 1$ are indeed allowed by the laws of thermodynamics. Here the consequences of this discovery for the theory of critical phenomena will be explored while more general and experimental consequences have been discussed elsewhere.[17]

2. Thermodynamics

2.1. *Refined thermodynamic classification scheme*

Let me begin by recalling the definition of the generalized order of a transition[3,4] as well as some of the mathematical requirements of thermodynamics.[18–22] The energy function $U(S, V, N)$ must be a single-valued, convex, monotonically increasing and almost everywhere differentiable function which is homogeneous of degree 1 and has the coordinates S, entropy, V, volume, and N particle number. Classically the state variables satisfy $0 \leq V < \infty$, $0 \leq N < \infty$, $-\infty < S < \infty$, 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.

The classification of phase transitions is usually discussed in terms of the free energy density or the pressure p.[1,3,4] The pressure is the *conjugate convex function*[24] to the energy density $u(s, \rho) = U(S/V, 1, N/V)/V$ as a function of entropy density $s = S/V$ and particle number density $\rho = N/V$ according to

$$p(T, \mu) = \sup_{s,\rho}(\mu\rho + Ts - u(s, \rho)) \tag{2.1}$$

where μ denotes the chemical potential and T the temperature. The existence of phase transitions requires the thermodynamic limit $V \to \infty$ to be taken appropriately. Consider a thermodynamic process $\mathcal{C} : \mathbb{R} \to \mathbb{R}^2$, $\sigma \mapsto (T(\sigma), \mu(\sigma))$ parametrized by σ such that $T(\sigma = 0) = T_c$, $\mu(\sigma = 0) = \mu_c$ corresponds to a critical point. The classification scheme for phase transitions[3,4] is based on the fractional derivatives[25]

$$\begin{aligned}\mathfrak{F}(\mathcal{C}, q; \sigma) &= \frac{d^q p_{\text{sng}}(T(\sigma), \mu(\sigma))}{d\sigma^q} \\ &= \lim_{N\to\infty} \Gamma(-q)^{-1} \left(\frac{|\sigma|}{N}\right)^{-q} \\ &\quad \times \sum_{j=0}^{N-1} \frac{\Gamma(j-q)}{\Gamma(j+1)} p_{\text{sng}}\left(T\left(\sigma - \frac{j\sigma}{N}\right), \mu\left(\sigma - \frac{j\sigma}{N}\right)\right) \end{aligned} \tag{2.2}$$

of the singular part of the pressure $p = p_{\text{reg}} + p_{\text{sng}}$. In Ehrenfests original classification scheme[26] a phase transition was defined to be of order $n^{\pm} \in \mathbb{N}$ iff

$$\mathfrak{F}(\mathcal{C}, n; \sigma) \sim A\Theta(\sigma) + B \tag{2.3}$$

for $\sigma \approx 0$ where $A, B \in \mathbb{R}$ and $\Theta(\sigma)$ denotes the Heaviside step function defined as $\Theta(\sigma) = 1$ for $\sigma > 0$ and $\Theta(\sigma) = 0$ for $\sigma < 0$. Equation (2.3) expresses a finite jump discontinuity in the n-th order derivative of the pressure.

In Refs. 3 and 4 the classification scheme of Ehrenfest was generalized by extending the order n from integers to real numbers. A phase transition was defined to be of order $\lambda^{\pm} \in \mathbb{R}$ iff

$$\lambda^{\pm}(\mathcal{C}) = \sup\{q \in \mathbb{R} | \lim_{\sigma\to 0^{\pm}} \mathfrak{F}(\mathcal{C}, q; \sigma) < \infty\} \tag{2.4}$$

which is sufficiently general to allow confluent logarithmic singularities. Note that the order will in general depend upon the particular choice of thermodynamic process $\mathcal{C}$. A phase transition of order λ implies that $\mathfrak{F}$ behaves asymptotically like a power function (of index λ) upon approach to the critical point.[3,4] This observation relates the order of the transition to the critical exponents as

$$\lambda_\varepsilon = 2 - \alpha_\varepsilon = 2 - \alpha \tag{2.5a}$$

$$\lambda_\Psi = 2 - \alpha_\Psi = 1 + 1/\delta \tag{2.5b}$$

where λ_ε denotes the thermal order and λ_Ψ the order along the direction of the field conjugate to the order parameter. In Eq. (2.5) $\alpha_\varepsilon = \alpha$ and $\alpha_\Psi = 1 - 1/\delta$ are the thermodynamic fluctuation exponents for the energy density ε and the order parameter density Ψ in Fishers notation,[6,27] while δ denotes the equation of state exponent and α the specific heat exponent.

In this paper a mathematically more refined classification scheme will be introduced based on the observation that the function $\mathfrak{F}(\mathcal{C}, n; \sigma)$ in Ehrenfests scheme (2.3) is a slowly varying function[28] of σ. A function $\Lambda(x)$ is called *slowly varying at infinity* if it is real-valued, positive and measurable on $[A, \infty)$ for some $A > 0$, and if

$$\lim_{x\to\infty} \frac{\Lambda(bx)}{\Lambda(x)} = 1 \tag{2.6}$$

for all $b > 0$. A function $\Lambda(x)$ is called *slowly varying at zero* if $\Lambda\left(\frac{1}{x}\right)$ is slowly varying at infinity.[28,29] The function $\mathfrak{F}(\mathcal{C}, n; \sigma)$ in (2.3) is slowly varying for $\sigma \to 0^+$ as well as for $\sigma \to 0^-$. Therefore in this paper *a phase transition is defined to be of order* $\lambda^\pm$ iff

$$\lim_{\sigma\to\pm\infty} \frac{\mathfrak{F}(\mathcal{C}, \lambda^\pm; b/\sigma)}{\mathfrak{F}(\mathcal{C}, \lambda^\pm; 1/\sigma)} = 1 \tag{2.7}$$

for all $b > 0$. This means that $\mathfrak{F}(\mathcal{C}, \lambda^\pm; \sigma)$ varies slowly as a function of σ for $\sigma \to 0^\pm$. The generalized order in this *refined classification scheme* is the same as in the scheme (2.4) because every slow varying function $\Lambda(x)$ has the property that $\lim_{x\to 0} x^{-\varepsilon}\Lambda(x) = \infty$ and $\lim_{x\to 0} x^{\varepsilon}\Lambda(x) = 0$ for all $\varepsilon > 0$.

In the refined classification scheme (2.7) each phase transition is classified by its generalized left and right orders $\lambda^\pm$ and functions $\Lambda^\pm$ which are slowly varying at the critical point. The classification scheme allows to distinguish also differences between transitions having the same order. The two dimensional Ising model is of second order $(\lambda, \Lambda) = (2, \log)$ while the mean field theory will be classed as second order $(\lambda, \Lambda) = (2, \Theta)$ where Θ denotes that Heaviside step function defined above.

Phase transitions of order $\lambda = 2$ occupy a special place in the thermodynamic classification scheme because they are self conjugate under Legendre transformation as will be shown next. Consider a thermal phase transition of order (λ, Λ) for $\tau \to 0^+$ in $p(\tau, \mu)$ where $\tau = (T - T_c)/T_c$ and $\mu = \mu_0$ is constant. Then $p(\tau)$ behaves as

$$p(\tau) \sim \tau^\lambda \Lambda(\tau) \tag{2.8}$$

for $T \to T_c^+$ where $\Lambda(\tau)$ is slowly varying for $\tau \to 0^+$. Define a slowly varying function $L(x)$ through

$$\Lambda(x) = \frac{1}{\lambda} L^{\frac{\lambda-1}{\lambda}}(x^\lambda) \,. \tag{2.9}$$

It is a standard result in the theory of slowly varying functions that for $\lambda > 1$ the conjugate convex function $u(\sigma) = \sup_\tau(\tau\sigma - p(\tau))$ behaves as

$$u(\sigma) \sim \frac{1}{\lambda^*} \sigma^{\lambda^*} L^{*\frac{\lambda^*-1}{\lambda^*}}(\sigma^{\lambda^*}) \tag{2.10}$$

for $\sigma \to 0^+$ where $\lambda^* > 1$ is given by

$$\lambda^* = \frac{\lambda}{\lambda - 1} \tag{2.11}$$

and $L^*(x)$ is the slowly varying function conjugate to $L(x)$.[29] For every $L(x)$ slowly varying at zero there exists a *conjugate slowly function* $L^*(x)$ which is defined such that

$$\lim_{x \to 0} L(x)L^*(xL(x)) = 1 \tag{2.12}$$

$$\lim_{x \to 0} L^*(x)L(xL^*(x)) = 1 \tag{2.13}$$

$$L^{**}(x) \sim L(x) \text{ for } x \to 0 \, . \tag{2.14}$$

$L^*(x)$ is asymptotically unique in the sense that if there exists another slowly varying function $L'(x)$ with the properties (2.12)–(2.14) then $L'(x) \sim L^*(x)$ for $x \to 0$. Thus to every phase transition of order (λ, Λ) in the pressure there corresponds a conjugate transition in the energy density which is of order (λ^*, Λ^*) with λ^* given by (2.11) and Λ^* related to L^* as Λ to L in (2.9). Phase transitions of order $\lambda = 2$ are *selfconjugate* in the sense that $\lambda = \lambda^*$. Phase transition of order $\lambda = 1$ are conjugate to transitions of order $\lambda^* = \infty$ and represent a special limiting situation.

2.2. *Anequilibrium phase transitions*

This section turns to the question posed in the introduction whether phase transitions of order $\lambda < 1$ are thermodynamically permissible. Consider $u(s, \rho)$ for a thermodynamic process in which the density $\rho = N/V$ is kept constant and which crosses a critical point at s_c. If the phase transition at s_c is of order $\lambda = \lambda^+ = \lambda^-$ then $u(s)$ has the form

$$u(s) = u_{\text{reg}}(s) + u^{\pm}(s)|s - s_c|^{\lambda} \tag{2.15}$$

where $u_{\text{reg}}(s)$ denotes the regular part and $u^{\pm}(s)$ varies slowly near s_c. Consequently any phase transition with $s_c < \infty$ and order $\lambda < 1$ violates the requirement of convexity for u or the condition $u < \infty$ (for $\lambda < 0$), and is thus forbidden by the laws of thermodynamics. This appears to restrict thermodynamically admissible transitions to the range $\lambda \geq 1$.

Although the restrictions on the thermodynamic state variables require a finite entropy or energy density, i.e., $s < \infty$ or $u < \infty$, the laws of thermodynamics do not require $s_c < \infty$, i.e., finiteness for the critical point. In fact the simplest solid-fluid phase diagrams in the (s, v)-plane are consistent with a critical point at $s_c = \infty$ separating the solid single phase region from the fluid single phase region. Such infinite entropy density transitions are not ruled out by the mathematical

requirements specified in the previous section. This can be demonstrated by giving an explicit counterexample to the contrary proposition. Such a counterexample is the following single-valued, continuous and differentiable energy density function

$$u(s) = as + b(s^2 + c^2)^{1/2} \tag{2.16}$$

where a, b, $c > 0$ and $a > b$. Clearly $T(s) = \frac{\partial u}{\partial s} > 0$ and $\frac{\partial^2 u}{\partial s^2} > 0$ and thus $u(s)$ is convex and monotonically increasing. $u(s)$ fulfills all requirements for the energy density of a thermodynamically stable system. Note that $u(s)$ exhibits transitions of order $\lambda_u^{\pm} = 1$ at $s_c = \pm\infty$. Moreover the thermodynamic system described by Eq. (2.16) has the curious property that the set of possible temperatures is restricted to the range

$$a - b = T_{\min} < T < T_{\max} = a + b \tag{2.17}$$

The pressure obtained from Eqs. (2.1) and (2.16) reads

$$p(T) = [c^2(b^2 - (T - a^2)^2)]^{1/2} \tag{2.18}$$

and it becomes complex outside the restricted temperature range (2.17). The pressure (2.18) has transitions of order $\lambda_p^{\pm} = 1/2$ at $T_{\min}$ and $T_{\max}$ respectively. More generally transitions of order $\lambda_u > 0$ in u are related to transitions of order

$$\lambda_p = \frac{\lambda_u}{\lambda_u + 1} \tag{2.19}$$

in p.[5] Note that now $0 < \lambda_p < 1$ while $0 < \lambda_u < \infty$.

The simple example (2.16) demonstrates that thermodynamics allows two fundamentally different types of phase transitions. On the one hand traditional phase transitions of order $\lambda_p^{\pm} \geq 1$ and on the other hand unusual phase transitions of order $0 < \lambda_p^{\pm} < 1$ for which the set of possible equilibrium temperatures appears to be restricted to a subset of the absolute temperature scale. The interest in this observation derives from the fact that equilibrium thermodynamics formally admits transitions whose presence would restrict its own applicability in the sense that the limiting critical temperatures $T_{\min}$ and $T_{\max}$ cannot be reached in any quasistatic process. A quasistatic process is a sequence of state changes which proceeds infinitely slowly compared to the time scale for the establishment of equilibrium. This raises the question whether the identification of the absolute temperatures scale with the ideal gas temperature scale remains valid when $\lambda < 1$ transitions are present. In such systems $T_{\min}$ plays the role of absolute zero and $T_{\max}$ that of $T = \infty$. In Ref. 5, it was suggested to circumvent the self-limitation to a finite temperature range through multivalued thermodynamic potentials and phase transitions of order $\lambda < 1$ were called nonequilibrium phase transitions because transitions between different sheets cannot occur quasistatically. The present paper however restricts all thermodynamic functions to remain single valued. In order to avoid confusion with standard literature usage of the terminus "nonequilibrium

phase transitions" I will use instead the word *anequilibrium phase transition* from now on.

The entropy density $s(T) = \left(\frac{\partial p}{\partial T}\right)_\mu$ derived from (2.18) diverges to $-\infty$ as $T \to T^+_{\min}$. Therefore the third law implies the existence of another special temperature T_0 defined by the condition

$$s(T_0) = 0 \tag{2.20}$$

of vanishing entropy density. Because the third law is of quantum mechanical origin the temperature T_0 is expected to be the minimal temperature for quantum systems while $T_{\min}$ is the minimal temperature for classical systems. Clearly $T_0 > T_{\min}$ is always fulfilled.

3. Statistical Mechanics

3.1. *Ensemble limit*

Given the thermodynamic classification of phase transition it is natural to ask whether anequilibrium phase transitions and a statistical mechanical classification corresponding to the thermodynamic scheme exist for critical behavior in statistical mechanics. These questions are discussed in the following sections. Statistical Mechanics for noncritical systems is based on the law of large numbers.[30] This suggests that the theory of critical phenomena may be founded in the theory of stable laws. Although natural this idea is usually rejected because the divergence of correlation lengths and susceptibilities appears to imply that the microscopic random variables are strongly dependent[31,32,33] while the standard theory of stable laws applies only to weakly dependent or independent variables.[28,34,35]

The problem of strong dependence arises from the particular choice of performing the infinite volume limit and the continuum limit. One usually starts from an infinite volume lattice theory and then ask for possible continuum (or scaling) limits of the rescaled infinite volume correlation functions.[33] Depending on whether the rescaled correlation lengths remain finite or not one distinguishes the "massive" and the "massless" scaling limit but in either case the infinite volume limit has been performed before taking the scaling limit.

The idea of the present paper for basing a statistical classification of critical behavior on the theory of stable laws is related to that of finite size scaling[36–40] and uses a different method of taking infinite volume and continuum limits. Consider a d-dimensional simple cubic lattice with lattice spacing $a > 0$ in "block geometry", i.e., having finite side length $L < \infty$ in all d directions. Let X be a scalar observable associated with each lattice point. The lattice represents a discretization of a large but finite statistical mechanical system.[41] Because the system in all directions the correlation length ξ_X for fluctuations in X is also finite, i.e., $\xi_X(\Pi) < \infty$. Let the lengths a, L and the parameters Π of the statistical mechanical system be such that

$$0 < a \ll \xi_X(\Pi) \ll L < \infty\,. \tag{3.1}$$

Thus the system decomposes into a large number of uncorrelated blocks of linear extension ξ_X. The *ensemble limit* is defined as the simultaneous limit in which

$$a \to 0,\ L \to \infty,\ \Pi \to \Pi_c \text{ such that } \xi_X(\Pi) \to \xi_X(\Pi_c) < \infty\ . \tag{3.2a}$$

Two cases can be distinguished: In the *critical ensemble limit*

$$0 < \xi_X(\Pi_c) < \infty \tag{3.2b}$$

while for the *noncritical ensemble limit*

$$\xi_X(\Pi_c) = 0\ . \tag{3.2c}$$

If $N = (L/\xi_X)^d$ denotes the number of uncorrelated blocks of size ξ_X and $M = (\xi_X/a)^d$ is the number of sites in each block then $NM = (L/a)^d$ is the total number of lattice sites. The correlation length ξ_X diverges in units of a in the critical ensemble limit but stays finite in the noncritical ensemble limit. Note also that $N \to \infty$ in the critical ensemble limit while N remains finite in the massive scaling limit or the finite size scaling limit.[37] The critical ensemble limit generates an infinite ensemble of uncorrelated blocks. This feature allows the application of standard limit theorems for uncorrelated or weakly dependent variables.

Let $X_{iN}(j)$ denote the scalar observable X at lattice site j ($j = 1, \ldots, M$) inside block i ($i = 1 \ldots, N$). Then

$$X_{iN} = \sum_{j=1}^{M} X_{iN}(j) \tag{3.3a}$$

are the *block sums* for block i and

$$X_N = \sum_{i=1}^{N} X_{iN} \tag{3.3b}$$

is the *ensemble sum* for the total system. The $X_{iN}(j)$ are random variables and so are X_{iN} and X_N. Let

$$\tilde{X}_N = (X_N - C_N)/D_N \tag{3.4}$$

denote the normed and centered ensemble sum and let $P_N(x) = \text{Prob}\{X_N < x\}$ be the probability distribution function of X_N. Assuming translation invariance the block variables are uncorrelated and identically distributed. Therefore the limiting distribution of $\tilde{X}_N$ is stable in the critical ensemble limit.[28,34,35] More precisely, if

$$P(x) = \lim_{N\to\infty} P_N(xD_N + C_N) \tag{3.5}$$

denotes the limiting distribution function of the normed ensemble sums (3.4) then the characteristic function $p(k) = \int_{-\infty}^{\infty} \exp(ikx) dP(x)$ of $P(x)$ has the representation

$$\log p(k) = iCk - D|k|^{\varpi}\left(1 - i\zeta \frac{k}{|k|}\omega(k, \varpi)\right) \tag{3.6}$$

where ϖ, ζ, C, D are constants whose ranges are

$$0 < \varpi \leq 2 \tag{3.7a}$$

$$-1 < \zeta \leq 1 \tag{3.7b}$$

$$-\infty < C < \infty \tag{3.7c}$$

$$D \geq 0 \tag{3.7d}$$

and

$$\omega(k, \varpi) = \begin{cases} \tan\left(\dfrac{\varpi\pi}{2}\right) & \text{for } \varpi \neq 1 \\ \dfrac{2}{\pi} \log |k| & \text{for } \varpi = 1 \end{cases} \tag{3.8}$$

The constant ϖ is called the *index* of the stable distribution while the parameter ζ characterizes its symmetry.

If the limit in (3.5) exists and $D > 0$ then the norming constants D_N must have the form[28,35]

$$D_N = N^{1/\varpi}\Lambda(N) \tag{3.9}$$

where the function $\Lambda(N)$ is slowly varying at infinity. The case $D > 0$ corresponds to the critical ensemble limit, while for $D = 0$ the limiting distribution $P(x)$ is degenerate, i.e., concentrated at a single point, corresponding to the noncritical ensemble limit.

The preceding limit theorem implies that in the limit $N \to \infty$ the distribution function of the ensemble sums can be approximated as

$$P_N(x) \approx P\left(\frac{x - C_N}{D_N}; \varpi, \zeta, C, D\right) \tag{3.10}$$

where the notation $P(x; \varpi, \zeta, C, D)$ is introduced for stable distributions of index ϖ. The objective in the next section will be to establish a large N scaling result for $P_N(x)$. To obtain it more information on the common distribution of the individual block variables is required.

The limiting distributions $\tilde{P}(x)$ of the individual block variables X_{iN} are independent of i because of translation invariance and they belong to the domain of attraction of a stable law. The class of possible block variable limits can thus be characterized as follows[35]: In order that the characteristic function $\tilde{p}(k)$ of $\tilde{P}(x)$ belong to the domain of attraction of a stable law whose characteristic function has logarithm $-D|k|^{\varpi}\left(1-i\zeta\frac{k}{|k|}\omega(k,\varpi)\right)$ with ϖ, ζ, D and $\omega(k,\varpi)$ as in (3.6)–(3.8) it is necessary and sufficient that in the neighborhood of the origin $k=0$

$$\log\tilde{p}(k)=i\tilde{C}k-D|k|^{\varpi}\tilde{\Lambda}(k)\left(1-i\zeta\frac{k}{|k|}\omega(k,\varpi)\right) \tag{3.11}$$

where $\tilde{C}$ is a constant and $\tilde{\Lambda}(k)$ is slowly varying function for $k\to 0$.

Equations (3.9) or (3.11) show that each ensemble limit $N, M\to\infty$ is labeled by a set of numbers ϖ, ζ, D with ranges as in (3.7) and a slowly varying function Λ. While D differentiates between critical and noncritical limits ϖ, ζ and Λ differentiate different critical ensemble limits. This characterization is reminiscent of the thermodynamic classification scheme and suggests a closer correspondence. To establish such a correspondence it is necessary to relate the generalized orders λ in the thermodynamical classification scheme to the numbers ϖ, ζ occurring in the characterization of ensemble limits. This will be done in the next section.

3.2. *Finite ensemble scaling*

The purpose of the present section is to investigate the N-dependence of the probability distribution for ensemble sums X_N is the limit of large N. The scaling relations emerging from this analysis will be called *finite ensemble scaling* because they are closely related to finite size scaling relations by virtue of the similarity between the critical ensemble limit defined above and the finite size scaling limit.[37] The question is how to choose the centering and norming constants C_N, D_N in (3.10) given the characterization (3.11) for the individual block variables X_{iN}.

The centering constants C_N in Eq. (3.10) can be eliminated from the problem by setting $C_N=-C'D_N$ where

$$C'=\begin{cases} C & \text{for } \varpi\neq 1\\ C+\dfrac{2}{\pi}\zeta D\log D & \text{for } \varpi=1\end{cases} \tag{3.12}$$

and with this choice (3.10) becomes

$$P_N(x)\approx P\left(\frac{x-C_N}{D_N};\varpi,\zeta,C,D\right)=P\left(\frac{x}{D^{1/\varpi}D_N};\varpi,\zeta,0,1\right) \tag{3.13}$$

Although the general form of D_N is known from (3.9) it remains to establish the relationship between the slowly varying functions in (3.9) and (3.11). Once this relation is established Eq. (3.13) represents a finite N scaling formula for a system in which the individual block variable limits are characterized by (3.11).

The limiting distribution functions of the individual block variables X_{iN} have characteristic functions as given by (3.11). Introduce

$$R(k) = |k|^{\varpi} \mathfrak{L}(k^{\varpi}) \tag{3.14}$$

where the slowly varying function $\mathfrak{L}(x)$ is defined through

$$\tilde{\Lambda}(k) = \mathfrak{L}(k^{\varpi}) \tag{3.15}$$

and $\tilde{\Lambda}(k)$ is the slowly varying function appearing in (3.11). For sufficiently large N the norming constants D_N are chosen as

$$D_N^{-1} = \inf \left\{ k > 0 : R(k) = \frac{D}{N} \right\} \tag{3.16}$$

which is possible because $R(k) \to 0$ for $k \to 0$ and $R(k)$ is continuous in a neighborhood of zero. Then for small k[35]

$$\lim_{N\to\infty} \left\{ \tilde{p}\left(\frac{k}{D_N}\right) \right\}^N = \lim_{N\to\infty} \exp\left\{ -NR\left(\frac{1}{D_N}\right) \frac{R\left(\frac{k}{D_N}\right)}{R\left(\frac{1}{D_N}\right)} \left(1 + i\zeta \frac{k}{|k|}\omega(k, \varpi)\right) \right\}$$

$$= \exp\left\{ -D|k|^{\varpi} \left(1 + i\zeta \frac{k}{|k|}\omega(k, \varpi)\right) \right\} . \tag{3.17}$$

It follows that $D \approx NR(1/D_N)$ for sufficiently large N and this determines D_N in terms of $\tilde{\Lambda}(k)$ and ϖ as

$$D_N = \left(\frac{N}{D\mathfrak{L}^*(N^{-1})} \right)^{\frac{1}{\varpi}} \tag{3.18}$$

where $\mathfrak{L}^*(x)$ is the conjugate slowly varying function to $\mathfrak{L}(x)$ defined in Eq. (3.15). The slowly varying function $\Lambda(N)$ appearing in (3.9) is thus given as

$$\Lambda(N) = \left(D\mathfrak{L}^*\left(\frac{1}{N}\right) \right)^{-\frac{1}{\varpi}} . \tag{3.19}$$

in terms of the limiting distributions (3.11) for the individual blocks.

Finally Eq. (3.13) gives the finite ensemble scaling for the distribution of ensemble variables X_N in the large N limit

$$P_N(x) = P\left(\frac{x\mathfrak{L}^{*1/\varpi}(N^{-1})}{N^{1/\varpi}}; \varpi, \zeta, 0, 1\right) . \tag{3.20}$$

More interesting than the ensemble variables X_N are the *ensemble averages* defined as $\bar{X}_N = \frac{X_N}{NM}$. The probability distribution function $\bar{P}_N(\bar{x})$ for the ensemble averages $\bar{X}_N$ has the finite ensemble scaling form

$$\bar{P}_N(\bar{x}) = \bar{P}\left(\frac{\bar{x}\mathfrak{L}^{*1/\varpi}(N^{-1})}{N^{(1-\varpi)/\varpi}}; \varpi, \zeta, 0, 1\right) . \tag{3.21}$$

Equations (3.20) and (3.21) are the central results of this paper. If $N = (L/\xi_X)^d$ is expressed in terms of the system size L they are seen to be closely related to finite size scaling theory. They are new inasmuch as they are derived without reference to a particular model or approximate critical Hamiltonian such as the Landau-Ginzburg-Wilson Hamiltonian. Equations (3.20) and (3.21) are valid for all translation invariant critical systems, i.e., systems for which the basic limit distribution (3.5) is not degenerate. They represent a general and model independent derivation of scaling in statistical mechanics without renormalization group theory.

3.3. *Identification of exponents and statistical classification scheme*

It is now possible to consider the correspondence between the statistical classification in terms of ϖ, ζ and $\tilde{\Lambda}$ and the thermodynamic classification in terms of λ and Λ. To do this the index ϖ in (3.20) and (3.21) must be related to the critical exponents. This is immediately possible from (3.21) by considering for example the order parameter Ψ. Setting $X = \Psi$, taking the derivative with respect to $\bar{x}$ in Eq. (3.21) and using $N = (L/\xi_\Psi)^d$ one finds that the k-th moment $\langle\overline{\Psi}^k\rangle$ of the order parameter scales with system size as $\langle\overline{\Psi}^k\rangle \sim L^{kd(\varpi-1)/\varpi}$. Comparing to standard finite size scaling theory[36–40] relates ϖ to the thermodynamic exponents as

$$\varpi_\Psi = \frac{\gamma + 2\beta}{\gamma + \beta} = 1 + \frac{1}{\delta} = \lambda_\Psi \tag{3.22}$$

where β and γ are the order parameter and susceptibility exponents, and λ_Ψ was defined in (2.5). Similarly for the energy density $X = \varepsilon$ one finds

$$\varpi_\varepsilon = 2 - \alpha = \lambda_\varepsilon \tag{3.23}$$

where λ_ε is the thermal order of (2.5). This suggests that the correspondence between the statistical and the thermodynamic classification of phase transition

is given generally as $\varpi = \lambda$. Note that second order (i.e., selfconjugate) phase transition occupy again a special case in the statistical classification scheme because of the bound $\varpi \leq 2$ in (3.7a). This fact will be related below to violations of hyperscaling relations.

The general identification $\lambda = \varpi$ implies that anequilibrium phase transitions with order $\lambda < 1$ correspond to stable limit distributions with index $\varpi < 1$. Thus anequilibrium transitions are not only found in equilibrium thermodynamics but also in equilibrium statistical mechanics. The fact that anequilibrium transitions restrict the range of equilibrium temperatures as in (2.17) is mirrored by the fact that thermal expectation values diverge in the critical ensemble limit for anequilibrium critical points with $\varpi < 1$. This implies that the traditional formulation of statistical mechanics becomes inapplicable at anequilibrium critical points just as traditional thermodynamics becomes inapplicable.

While the general correspondence between $\lambda < 1$ and $\varpi < 1$ is reassuring it is not sufficient to establish the existence of anequilibrium phase transition in statistical mechanics. To demonstrate their existence requires a possibly exact calculation of the partition sum for a concrete statistical mechanical model. It is surprisingly simple to demonstrate the existence of anequilibrium transitions in this way. A concrete example occurs in what is perhaps the simplest model in the theory of critical phenomena, namely the one dimensional Gaussian model.[41] This finding is particularly interesting because the Gaussian model is of central importance in the modern theory of critical phenomena as the starting point for systematic perturbative calculations.[6] The model Hamiltonian is $\mathcal{H} = -\frac{J}{2}\sum \Psi_i \Psi_j$ where the sum runs over all nearest neighbour pairs of lattice sites i, j and the continuous spin variables Ψ_i have a Gaussian single spin measure proportional to $\exp[-\sigma\Psi_i^2]$. The limiting free energy density for the one dimensional Gaussian model is well known and it reads

$$-\frac{f(T)}{k_B T} = \frac{1}{2}\log \pi - \frac{1}{2}\log\left(\frac{1}{2}(\sigma + (\sigma^2 - K^2)^{1/2}\right) \tag{3.24}$$

where $K = \frac{J}{k_B T}$ and k_B denotes Boltzmann's constant. The exact free energy density (3.24) for the one dimensional Gaussian model exhibits an anequilibrium transition of order $\lambda_\varepsilon = \frac{1}{2}$ at the critical temperature $T_{\min} = \frac{J}{k_B \sigma}$.

3.4. *General mechanism for the violation of hyperscaling*

The identification $\lambda = \varpi$ obviously cannot hold for all values of $\lambda > 0$ because $\varpi \leq 2$ is required by (3.7). The new restriction $\varpi \leq 2$ is readily seen to be related to the violation of hyperscaling and the breakdown of finite size scaling for thermal fluctuations in dimensions $d > 4$. To see this consider the class of statistical mechanical models obeying the Lebowitz inequality for the four point functions and infrared bounds for the two point functions.[33] For such models the susceptibility exponent γ obeys $\gamma \geq 1$ and the correlation function exponent η obeys $\eta \geq 0$.

Then using $\varpi_\varepsilon \leq 2$, the Fisher inequality $\gamma \leq (2-\eta)\nu$, the hyperscaling relation $d\nu = 2 - \alpha$ and relation (3.23) the following chain of inequalities is obtained.

$$d \leq d\gamma \leq (2-\eta)d\nu = (2-\eta)(2-\alpha) = (2-\eta)\varpi_\varepsilon \leq 2(2-\eta) \leq 4 \,. \qquad (3.25)$$

In the general situation hyperscaling may fail only at $\varpi = 2$ because only the domain of attraction of the normal law contains nonscaling limit distributions. Note that in this way the inequality $\varpi \leq 2$ provides a general mechanism for the breakdown of hyperscaling independent of identifying dangerous irrelevant variables in a particular model. Analogous breakdown phenomena are expected to occur for critical fluctuations in observables other than the energy density.

4. Temperature Renormalization

The presence of anequilibrium transitions in a statistical mechanical system $\mathfrak{S}$ implies strong fluctuations. In fact at the transition point the fluctuations become so strong that a canonical or thermodynamical equilibrium description of the system becomes impossible because the ensemble averaged energy or entropy diverges in the infinite system. The underlying microscopic dynamics however remains well defined in terms of a classical or quantum mechanical microscopic Hamiltonian. The total energy of the system is well defined and conserved and the system can be described microcanonically. If the system $\mathfrak{S}$ undergoes anequilibrium transitions at $T^{\mathfrak{S}}_{\min}$ and $T^{\mathfrak{S}}_{\max}$ then heating or cooling across $T^{\mathfrak{S}}_{\min}$ and $T^{\mathfrak{S}}_{\max}$ cannot occur quasistatically and the system must fall out of equilibrium when attempting it.

Consider now the usual setup for the canonical ensemble in which $\mathfrak{S}$ is weakly coupled to a reservoir $\mathfrak{R}$. What happens if the reservoir itself undergoes anequilibrium transitions at $T^{\mathfrak{R}}_{\min}$ and $T^{\mathfrak{R}}_{\max}$? Clearly, the combined system $\mathfrak{R} \cup \mathfrak{S}$ has a hamiltonian description and can always be treated in the microcanonical ensemble. But what happens to a canonical description? One expects that the canonical description should remain applicable as long as $T^{\mathfrak{R}}_{\min}$ is very small and $T^{\mathfrak{R}}_{\max}$ very large, i.e., for $\frac{T^{\mathfrak{R}}_{\min}}{T} \ll 1 \ll \frac{T^{\mathfrak{R}}_{\max}}{T}$, while the temperature dependence of the results should become modified otherwise. The temperature dependence of the results of canonical calculations enters through the Lagrange parameter $\beta(T)$ for the average energy. The Lagrange parameter β appearing in the canonical and the grand canonical ensembles is a universal (i.e., $\mathfrak{S}$-independent) function of absolute temperature T and at the same time a property of the reservoir $\mathfrak{R}$. In fact if the reservoir $\mathfrak{R}$ consists of a large number of weakly interacting subsystems (e.g., particles) then β^{-1} is proportional to the limiting energy per subsystem of $\mathfrak{R}$.[30] Because β is related to the energy density of the reservoir unusual temperature dependence must be expected whenever the substance of the reservoir itself undergoes anequilibrium transitions. If the reservoir is described quantum mechanically then $T^{\mathfrak{R}}_0$ defined by Eq. (2.20) will be the lowest temperature of the reservoir corresponding to the ground state of the

reservoir Hamiltonian. For classical reservoirs $T^{\mathfrak{R}}_{\min}$ will be the lowest temperature. If the reservoir has no anequilibrium transitions, i.e., if $T^{\mathfrak{R}}_0 = 0$ and $T^{\mathfrak{R}}_{\max} = \infty$ then the temperature dependence must have the usual universal form

$$\beta(T) = \frac{1}{k_B T} \,. \tag{4.1}$$

If however $T^{\mathfrak{R}}_0 > 0$ and $T^{\mathfrak{R}}_{\max} < \infty$ the form (4.1) cannot be correct. The energy per subsystem of the reservoir is proportional to β^{-1} and it diverges as T approaches $T^{\mathfrak{R}}_{\max}$. Thus for finite $T^{\mathfrak{R}}_{\max} < \infty$ one must have

$$\beta(T^{\mathfrak{R}}_{\max}) = 0 \tag{4.2}$$

and this contradicts (4.1) because $\frac{1}{k_B T^{\mathfrak{R}}_{\max}} > 0$. Similarly

$$\beta^{-1}(T^{\mathfrak{R}}_0) = 0 \tag{4.3}$$

also violates (4.1) because $T^{\mathfrak{R}}_0 > T^{\mathfrak{R}}_{\min} > 0$. To satisfy the relations (4.2) and (4.3) the temperature T and the parameter β must in general become renormalized into

$$`T = T - T^{\mathfrak{R}}_0 \tag{4.4}$$

$$`\beta = \beta - \beta(T^{\mathfrak{R}}_{\max}) \tag{4.5}$$

whenever the reservoir undergoes anequilibrium transitions. This suggests that canonical averages $\langle \mathcal{O} \rangle$ of an observable $\mathcal{O}$ will in general depend on temperature through (4.4) and (4.5). For classical reservoirs $T^{\mathfrak{R}}_0$ in (4.4) has to be replaced by $T^{\mathfrak{R}}_{\min}$. Equations (4.4) and (4.5) are general predictions for the temperature dependence of canonical averages in systems with anequilibrium transitions resulting from requiring consistency for the interpretation of β. Clearly these general results are corroborated by the explicit solution (3.24) for the Gaussian model.

The main result expressed in (4.4) and (4.5) is the fact that the temperature dependence of canonical averages depends on the nature of the reservoir with which the system is equilibrated whenever the reservoir undergoes phase transitions of order less than one. Note that in every theoretical evaluation of a canonical partition sum it is implicitly assumed that the system can be equilibrated with a reservoir $\mathfrak{R}$ such as an ideal gas with $T^{\mathfrak{R}}_0 = 0$ and $T^{\mathfrak{R}}_{\max} = \infty$ not undergoing nonequilibrium transitions. This implicit assumption need not be fulfilled in experiment. In fact experimentally the reservoir is very often of the same material as the system itself because the system under study is part of a much larger (ideally infinite) sample. In that case $T^{\mathfrak{R}}_0 = 0 = T^{\mathfrak{S}}_0$ and $T^{\mathfrak{R}}_{\max} = T^{\mathfrak{S}}_{\max}$ and unusual temperature dependence must be expected as T approaches $T^{\mathfrak{S}}_0$.

5. Conclusion

The paper has discussed the recent classification theory of phase transitions[3–5] in greater detail. In particular the original thermodynamic classification scheme[3,4] has been refined, and the statistical classification scheme suspected in Ref. 5 has been identified. First and second order phase transitions play special roles in both classification schemes. The paper presents the first model-independent derivation of scaling in statistical mechanics which is not based on renormalization group theory. A new and general mechanism for violations of hyperscaling (and finite size scaling) has been identified. The classification theory predicts the existence of phase transitions with orders less than unity. A concrete example is shown to be realized in the one dimensional Gaussian model. The presence of such transitions implies a dependence of β on the nature of the reservoir. As discussed elsewhere[17] anequilibrium transitions are expected to exist in experiment.

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References

1. M. E. Fisher and G. W. Milton, *Physica* **138A**, 22 (1986).
2. M. E. Fisher, *Proceedings of the Gibbs Symposium* (American Mathematical Society, 1990), pp. 39.
3. R. Hilfer, *Physica Scripta* **44**, 321 (1991).
4. R. Hilfer, *Phys. Rev. Lett.* **68**, 190 (1992).
5. R. Hilfer, *Mod. Phys. Lett.* **B6**, 773 (1992).
6. M. E. Fisher, in *Critical Phenomena*, ed. F. J. W. Hahne (Springer, Berlin, 1983), pp. 1.
7. A. Coniglio and M. Zanetti, *Europhys. Lett.* **10**, 575 (1989).
8. P. Meakin, A. Coniglio, H. E. Stanley, and T. A. Witten, *Phys. Rev.* **A34**, 3325 (1986).
9. A. Coniglio and M. Zanetti, *Phys. Rev.* **B42**, 6873 (1990).
10. A. Coniglio and M. Zanetti, *Physica* **163A**, 325 (1990).
11. L. P. Kadanoff, S. R. Nagel, L. Wu. and S. M. Zhou, *Phys. Rev.* **A39**, 6524 (1989).
12. X. Z. Wu, L. P. Kadanoff, A. Libchaber, and M. Sano, *Phys. Rev. Lett.* **64**, 2140 (1990).
13. L. Wu, P. K. Dixon, S. R. Nagel, B. D. Williams, and J. P. Carini, *Phys. Rev. Lett.* **65**, 1108 (1990).
14. M. H. Jensen, G. Paladin and A. Vulpiani, *Phys. Rev. Lett.* **67**, 208 (1991).
15. U. Frisch and M. Vergassola, *Europhys. Lett.* **14**, 439 (1991).
16. C. Amitrano, A. Coniglio, P. Meakin, and M. Zanetti, *Phys. Rev.* **B44**, 4974 (1991).
17. R. Hilfer, "Thermal field theory", *Nucl. Phys. B*, accepted for publication, R. Hilfer, "Classification theory for anequilibrium phase transition", *Phys. Rev. E*, in print.
18. A. S. Wightman, in *Convexity in the Theory of Lattice Gases*, ed. R. B. Israel (Princeton University Press, Princeton, 1979).

19. A. Martin-Löf, *Statistical Mechanics and the Foundations of Thermodynamics*, Lecture Notes in Physics Vol. 101 (Springer, Berlin, 1979).
20. H. B. Callen, *Thermodynamics and an Introduction to Thermostatics* (Wiley, New York, 1985).
21. R. Becker, *Theorie der Wärme*, 3. Aufl. (Springer, Berlin, 1985).
22. N. Straumann, *Thermodynamik*, Lecture Notes in Physics, Vol. 265 (Springer Berlin, 1986).
23. R. B. Griffiths and D. Ruelle, *Commun. Math. Phys.* **24**, 169 (1971).
24. A. W. Roberts and D. E. Varberg, *Convex Functions* (Academic Press, New York, 1973).
25. U. Westphal, *Proc. London Math. Soc. (3)* **29**, 557 (1974).
26. P. Ehrenfest, *Supplement No. 75b zu den Mitteilungen aus dem Kamerlingh* (Onnes-Institut, Leiden, 1933.
27. M. E. Fisher, in *Collective Properties of Physical Systems*, ed. B. Lundqvist and S. Lundqvist, *Proc. of 24th Nobel Symposium* (Academic Press, New York, 1973), p. 16.
28. W. Feller, *An Introduction to Probability Theory and Its Applications*, Vol. II (Wiley, New York, 1971).
29. E. Seneta, *Regularly Varying Functions* (Springer, Berlin, 1976).
30. A. I. Khinchin, *Mathematical Foundations of Statistical Mechanics* (Dover Publ., New York, 1949).
31. M. Cassandro and G. Jona-Lasinio, *Adv. in Physics* **27**, 913 (1978).
32. Ya. C. Sinai, *Theory of Phase Transitions: Rigorous Results* (Pergamon Press, Oxford, 1982).
33. R. Fernandez, J. Fröhlich and A. D. Sokal, *Random Walks, Critical Phenomena, and Triviality in Quantum Field Theory* (Springer, Berlin, 1992).
34. B. V. Gendenko and A. N. Kolmogorov, *Limit Distributions for Sums of Independent Random Variables* (Addison-Wesley, Cambridge, 1954).
35. I. A. Ibragimov and Yu. V. Linnik, *Independent and Stationary Sequences of Random Variables* (Wolters-Noordhoff, Groningen, 1971).
36. J. L. Cardy ed., *Finite Size Scaling* (North-Holland, Amsterdam, 1988).
37. E. Brezin and J. Zinn-Justin, *Nucl. Phys.* **B257**, 867 (1985). In the finite size scaling limit $L/a = NM \to \infty$, $\xi_X/a = M \to \infty$ simultaneously but $L/\xi_X = N < \infty$.
38. K. Binder, M. Nauenberg, V. Privman, and A. P. Young, *Phys. Rev.* **B31**, 1498 (1985).
39. V. Privman ed., *Finite Size Scaling and Numerical Simulation of Statistical Systems* (World Scientific, Singapore, 1990).
40. K. Binder, in *Computational Methods in Field Theory*, ed. H. Gausterer and C. B. Lang (Springer, Berlin, 1992) p. 59.
41. D. Ruelle, *Statistical Mechanics* (Benjamin Inc., London, 1969).
42. T. H. Berlin and M. Kac. *Phys. Rev.* **86**, 821 (1952).