Microcanonical entropy for small magnetizations

Microcanonical entropy for small magnetizations

Hans Behringer

Institut für Theoretische Physik I, Universität Erlangen-Nürnberg, D-91058 Erlangen, Germany

E-mail: Hans.Behringer@physik.uni-erlangen.de

Abstract
Physical quantities obtained from the microcanonical entropy surfaces of
classical spin systems show typical features of phase transitions already
in finite systems. It is demonstrated that the singular behaviour of the
microcanonically defined order parameter and susceptibility can be understood
from a Taylor expansion of the entropy surface. The general form of the
expansion is determined from the symmetry properties of the microcanonical
entropy function with respect to the order parameter. The general findings are
investigated for the four-state vector Potts model as an example of a classical
spin system.

PACS numbers: 05.50.+q, 64.60.−i, 75.10.−b

1. Introduction

The macroscopic behaviour of a physical system in thermodynamic equilibrium is related to
the microscopic properties by statistical mechanics. The basic quantity in this connection
is the density of states depending on the macroscopic quantities of interest. For a classical
spin system as a model system to describe magnetic properties, these macroscopic variables
are energy and magnetization. In the traditional approach to the statistical description of
phase transitions, the density of states is Laplace-transformed to the partition function which
is a concept of the canonical ensemble and the physics is deduced from the corresponding
potential, the Gibbs free energy. In recent years an alternative approach to analyse phase
transitions within a statistical framework has been developed in the microcanonical ensemble
(Gross 1986a, 1986b, 2001, Hüller 1994, Promberger and Hüller 1995, Gross *et al* 1996).
Apart from works on general questions of the equivalence and inequivalence of the various
ensembles (Lewis *et al* 1994, Dauxois *et al* 2000, Barré *et al* 2001, Ispolatov and Cohen
2001), and of the thermodynamic limit in the microcanonical ensemble (Kastner (2002) to cite
a recent work), second-order phase transitions have also been studied recently (Kastner *et al*
2000, Hüller and Pleimling 2002). Ways to extract critical exponents from microcanonical
quantities have been suggested (Kastner *et al* 2000, Hüller and Pleimling 2002). In these

works it was numerically demonstrated that the microcanonically defined physical quantities such as the microcanonical order parameter or the susceptibility exhibit singularities in finite systems. However, these numerical studies suggest that the microcanonical singularities are characterized by classical critical exponents in contrast to the non-trivial exponents showing up in the thermodynamic limit.

The aim of the present paper is to provide an analytic understanding of the characterization of the singularities in physical quantities of finite microcanonical systems by classical exponents. To this end the entropy surface is expanded into a Taylor series in terms of its natural variable energy and magnetization and the asymptotic behaviour of the macroscopic quantities is investigated. This procedure is similar to the Landau expansion of the free energy of the infinite system although a striking difference has to be stressed. The Landau approach is an *approximation* of the free energy of the *infinite* canonical system whereas the treatment presented below is *exact* for the *finite* microcanonical system.

The paper is organized in the following way. Section 2 contains a short survey of the microcanonical approach to statistical mechanics. In particular the basic concepts and findings of the investigation of second-order phase transitions are summarized. In section 3 the appearance of the classical critical exponents is related to the analyticity of the thermodynamic potential of finite systems. Section 4 contains general considerations about the Taylor expansion of entropy surfaces with a C_{nv} order parameter symmetry. In addition, an investigation of the entropy surface of finite vector Potts models with four states is presented. The analysed data are obtained from Monte Carlo simulations.

2. Thermostatics in microcanonical systems

The analysis of statistical properties of classical spin systems within the microcanonical ensemble starts from the density of states

$$\Omega(E, M, L^{-1}) = \sum_{\sigma \in \Gamma_N} \delta_{E, \mathcal{H}(\sigma)} \delta_{M, \mathcal{M}(\sigma)}. \tag{1}$$

Here it is assumed that the system is defined on a d-dimensional hypercube of extension L. The Hamiltonian $\mathcal{H}$ gives the total energy of the microstate σ and the magnetization operator $\mathcal{M}$ gives its total magnetization. In general the magnetization is a multicomponent object $M = (M_1, \ldots, M_n)$. The microcanonical entropy is obtained by taking the logarithm of the density of states:

$$s(e, m, L^{-1}) = \frac{1}{L^d} \ln \Omega(E, M, L^{-1}). \tag{2}$$

To compare different system sizes the extensive factor L^d is divided to give the specific energy $e = E/L^d$ and the specific magnetization $m = M/L^d$. The dependence of the physical quantities on the system size L is suppressed in the following. The statistical properties of an isolated physical system are deduced from the entropy surface. The microcanonical spontaneous magnetization of a finite system for a fixed energy is defined by

$$m_{\mathrm{sp}}(e) : \Longleftrightarrow s(e, m_{\mathrm{sp}}(e)) = \max_m s(e, m) \tag{3}$$

hence $m_{\mathrm{sp}}(e)$ corresponds to the magnetization with the maximum entropy for a given energy.

The non-vanishing multicomponent spontaneous magnetization vector defines a direction in the order parameter space:

$$m_{\mathrm{sp}}(e) = \left(m_{\mathrm{sp}}^{(1)}(e), \ldots, m_{\mathrm{sp}}^{(n)}(e) \right) = |m_{\mathrm{sp}}(e)| m_0 \tag{4}$$

where m_0 is a fixed unit vector with several possible orientations below e_c. Note, however, that it might be possible that m_0 and consequently the associated orientations are themselves functions of energy below e_c. Let G_0 be the symmetry group of the microcanonical entropy with respect to the magnetization components, i.e.

$$s(e, g(m)) = s(e, m) \tag{5}$$

for all transformations g in G_0. If the spontaneous magnetization m_{sp} is finite, the symmetry group G_0 of the entropy is broken down to the subgroup $G < G_0$ that leaves the direction m_0 invariant (Behringer 2003).

In the microcanonical ensemble of isolated systems, no external magnetic field appears. However, magnetic fields can be defined as the conjugated variable of the magnetization components giving rise to the relation[1]

$$h_i(e, m_{sp}(e)) \frac{\partial}{\partial e} s(e, m_{sp}(e)) = -\frac{\partial}{\partial m_i} s(e, m_{sp}(e)) \tag{6}$$

for the ith component in equilibrium.

The susceptibility of the system is related to the curvature of the entropy along the magnetization direction. For a multicomponent magnetization, the curvature at the spontaneous magnetization is related to the Hessian

$$H_{kl}(e, m_{sp}(e)) = \frac{\partial^2}{\partial m_k \partial m_l} s(e, m_{sp}(e)) \tag{7}$$

of the entropy and the susceptibility is consequently a tensor which is given by

$$\chi_{ij}^{(0)}(e) = -\frac{\partial}{\partial e} s(e, m_{sp}(e)) (H^{-1}(e, m_{sp}(e)))_{ij}. \tag{8}$$

From a geometrical point of view, the specific heat of the system is connected to the curvature along the energy direction. At the spontaneous magnetization, the specific heat is given by

$$c^{(0)}(e) = -\frac{\left(\frac{\partial}{\partial e} s(e, m_{sp}(e))\right)^2}{\frac{\partial^2}{\partial e^2} s(e, m_{sp}(e))}. \tag{9}$$

Alternatively one can consider a specific heat that is more directly related to the canonical viewpoint where the specific heat is calculated from the canonical entropy

$$s_{can} = -\frac{\partial}{\partial T} g(T, h) \tag{10}$$

obtained from the Gibbs free energy $g(T, h)$ of the system in equilibrium as

$$c_{can} = T \frac{\partial}{\partial T} s_{can}. \tag{11}$$

Defining the equilibrium entropy by

$$\tilde{s}(e) = s(e, m_{sp}(e)) \tag{12}$$

one obtains the alternative specific heat

$$\tilde{c}(e) = -\frac{\left(\frac{d}{de} \tilde{s}(e)\right)^2}{\frac{d^2}{de^2} \tilde{s}(e)}. \tag{13}$$

---

[1] The sloppy but more convenient notation $\frac{\partial}{\partial x} f(x_0)$ for $\frac{\partial}{\partial x} f(x)|_{x=x_0}$ is used in the following, upper indices are not discriminated from lower ones.

The specific heat $\tilde{c}$ is different from $c^{(0)}$ as m_{sp} is first plugged into s and the derivative with respect to energy is worked out afterwards. In contrast, $c^{(0)}$ is evaluated as given in footnote 1.

From a statistical point of view, a phase transition from a disordered high-symmetric macrostate to an ordered low-symmetric macrostate is defined to take place at a non-analytic point of the corresponding thermostatic potential describing the properties of the physical system. Yang and Lee showed that the grand canonical thermostatic potential, i.e. the Gibbs free energy, is an analytic function for all finite system sizes (Yang and Lee 1952, Lee and Yang 1952). This means that a phase transition can only occur in the thermodynamic limit of an infinite system; according to the above definition, phase transitions are not possible in finite systems.

However, the microcanonical equilibrium quantities exhibit typical features of phase transitions (Kastner *et al* 2000). For instance the microcanonical spontaneous magnetization (3) displays the characteristics of spontaneous symmetry breaking. This spontaneous magnetization defines the order parameter. For the high-energy phase the microcanonical order parameter is zero, reflecting a phase with high symmetry. The abrupt emergence of a finite-order parameter for low energies indicates the transition to an ordered phase with lower symmetry. The energy at which this onset occurs defines unambiguously the critical energy e_c of the finite microcanonical system. The susceptibility (8) of the system diverges at this energy.

The use of the expressions *critical* and *phase transition* to describe the behaviour of finite microcanonical systems is somewhat problematic as they are commonly used for certain properties of the infinite system. Nevertheless, the appearance of features of the microcanonical quantities which are also found in infinite systems at the transition point suggests its usage. Another delicate point is the discreteness of the physical quantities of discrete spin systems where the language used refers to continuous functions that most suitably describe the discrete data. In the microcanonical analysis of continuous spin systems e.g. the xy (Richer *et al* 2004) or the Heisenberg model, this concern does not exist.

The existence of a non-trivial spontaneous magnetization is in general related to the appearance of a convex dip in the microcanonical entropy. This is different in the canonical ensemble where the curvature along the natural variables is connected to the mean square deviation of a physical quantity. The curvature has therefore a well-defined sign. Although the physical quantities show singularities at the transition point that are typical of phase transitions, there is no phase transition as long as the microcanonical system is finite. The microcanonical entropy of finite systems is an analytic function of their natural variables and hence a phase transition in the mathematical sense defined above does not take place.

The singular behaviour of the order parameter with respect to the energy can, however, be described by means of a critical exponent (Kastner *et al* 2000). For a physical quantity $Q(e)$ of the finite system, this critical exponent, say $\tilde{\kappa}$, is defined by

$$\tilde{\kappa} = \lim_{e \to e_c} \frac{d \ln |Q(e)|}{d \ln |e - e_c|}. \tag{14}$$

The microcanonical critical exponent $\tilde{\beta}$ of the spontaneous magnetization in finite systems turns out to have the classical value $1/2$, the corresponding exponent $\tilde{\gamma}$ of the susceptibility is 1 for all system sizes. Both definitions (9) and (13) of the specific heat are characterized by the exponent $\tilde{\alpha} = 0$. Whereas the specific heat $c^{(0)}$ has a kink at the critical energy, $\tilde{c}$ exhibits a jump at e_c with different values $\tilde{c}(e_c^+) \neq \tilde{c}(e_c^-)$. The kink of $c^{(0)}$ at the critical energy with $c^{(0)}(e_c^+) = c^{(0)}(e_c^-)$, but different left-handed and right-handed derivatives at e_c, however, is not a cusp-singularity according to the definition of Stanley (1972) as the higher

order derivatives of $c^{(0)}$ do not diverge at e_c. Note also that both quantities tend to the same function in the thermodynamic limit.

3. Taylor expansion of the microcanonical entropy

For a finite system with the typical characteristics of a continuous phase transition, the microcanonically defined order parameter near the critical point vanishes like a square root. This behaviour can be understood in a Landau type of approach to the description of phase transitions in the microcanonical ensemble. To this end the entropy is expanded into a Taylor series as a function of the order parameter components. A proof of the analyticity of the microcanonical entropy is still lacking. Nevertheless, in view of the analyticity of the canonical thermostatic potential, it seems obvious to use this assumption. Note that this approach is exact provided the entropy of a finite system is an analytic function and hence can be expanded about any point (e, m) in the parameter space. This is different in the Landau theory of the free energy of the infinite system. In this approximation the Helmholtz free energy is assumed to be analytic although a phase transition in the thermodynamic limit is related to a non-analytic point in the thermostatic potential. Consequently, the critical behaviour obtained from the Landau approximation may differ from the true non-trivial behaviour of physical systems. This is indeed the case below the upper critical dimension.

The Taylor expansion of the microcanonical entropy of the finite system about the magnetization $m = 0$ (the equilibrium magnetization of the high-energy phase) yields the general series

$$s(e, m) = s(e, m = 0) + \sum_{(p_1, ..., p_n)} a_{p_1, ..., p_n}(e) \prod_i m_i^{p_i} \tag{15}$$

where the expansion coefficients are related to the derivatives of the entropy with respect to the magnetizations

$$a_{p_1, ..., p_n}(e) = \frac{1}{p_1! \cdots p_n!} \partial_{m_1}^{p_1} \cdots \partial_{m_n}^{p_n} s(e, m = 0). \tag{16}$$

The symmetry group G_0 of the entropy with respect to the magnetization determines which coefficients $a_{p_1, ..., p_n}$ appear in the expansion (15). Only the coefficients which correspond to monomials $m_1^{p_1} \cdots m_n^{p_n}$ that are invariant under the transformations $g \in G_0$ are in general non-zero, all other coefficients necessarily vanish. In view of the symmetry G_0, the expansion (15) is in fact an expansion in terms of the symmetry-adapted harmonics of the group G_0.

The physical behaviour for small magnetizations is already described by the low-order terms in (15). Suppose the magnetization is only one dimensional and the microcanonical entropy is left invariant by the transformation $m \to -m$. Note that these are the symmetry properties of the entropy of the Ising model. Then only even powers contribute to the Taylor expansion and, up to the fourth-order term, one gets

$$s(e, m) = s(e, 0) + \tfrac{1}{2}a(e)m^2 + \tfrac{1}{4}b(e)m^4. \tag{17}$$

As the maximum of the entropy must not be at an infinite magnetization, the coefficient of the highest power of m has to be negative. This requirement is indeed fulfilled for an Ising model in the energy interval about e_c where a finite-order parameter emerges. The Ising model is defined by the Hamiltonian

$$\mathcal{H} = -\sum_{\langle ij \rangle} \sigma_i \sigma_j \tag{18}$$

where the spins σ_i can be in the state $+1$ or -1 and the summation runs over neighbour pairs of spins. Figure 1 displays the derivatives $\partial_{m^q} s(e, 0)$ of a two-dimensional Ising model with
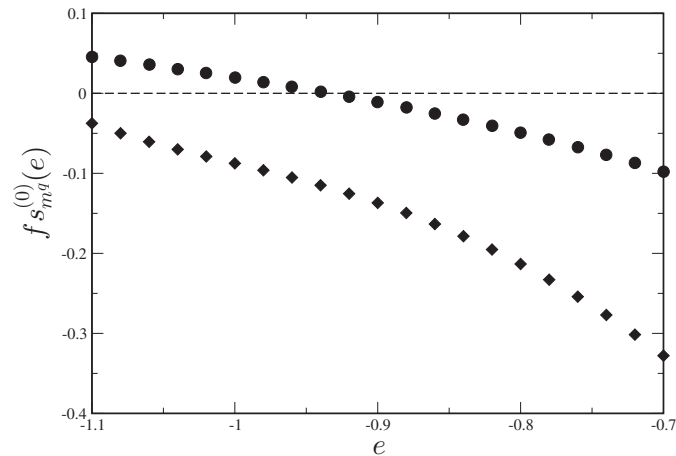
Figure 1. The derivatives $\partial_{m^2}s(e,0)$ and $\partial_{m^4}s(e,0)$ of the entropy surface of a two-dimensional Ising model with 200 spins in a square-lattice geometry. The fourth-order derivative is multiplied by a factor $f = 0.1$. The second-order derivative changes its sign at the transition energy $e_c = -0.934$ whereas the fourth-order derivative remains negative in the vicinity of e_c.

200 spins near the energy e_c. The underlying two-dimensional lattice has a square-lattice topology. The density of states of the system is evaluated numerically exact by a microcanonical transfer matrix method (Binder 1972, Creswick 1995) so that it is possible to reliably work out higher order derivatives. Condition (3) for thermostatic equilibrium leads to the equation

$$\frac{\partial}{\partial m}s(e,m) = m(a(e) + b(e)m^2) = 0 \tag{19}$$

for $m_{sp}(e)$. This relation always has the trivial solution $m_{sp}(e) = 0$ and in addition the solutions

$$m_{sp}(e) = \pm\sqrt{-\frac{a(e)}{b(e)}} \tag{20}$$

with a non-trivial, finite-order parameter if the coefficient $a(e)$ is positive. The stability condition

$$\frac{\partial^2}{\partial m^2}s(e, m_{sp}(e)) < 0 \tag{21}$$

is always satisfied for the non-trivial solution (20) provided it exists. The solution $m_{sp}(e) = 0$ is only stable, i.e. it corresponds to a maximum of the entropy, if the coefficient $a(e)$ is negative. The coefficient $a(e)$ changes its sign at the energy e_c. Hence the equilibrium magnetization of the entropy (17) is given by

$$m_{sp}(e) = \pm\Theta(a(e))\sqrt{\left|\frac{a(e)}{b(e)}\right|} \tag{22}$$

where the Heaviside function is denoted by Θ. As the coefficient $b(e)$ is negative in the vicinity of e_c and the two functions a and b are smooth, the order parameter varies continuously as a function of the energy e. Below the energy e_c it attains a finite value. Note that at the energy e_c the solution $m = 0$ becomes instable and the curvature of the entropy along the

magnetization changes its sign. The existence of two stable solutions below e_c signals the spontaneous breakdown of the global $m \to \pm m$ symmetry of the physical system. The depth

$$\Delta(e) = s(e, m_{sp}(e)) - s(e, 0) \tag{23}$$

of the convex dip along the magnetization for fixed energy can also be expressed in terms of the expansion coefficients of the entropy surface. Near the critical point of the finite system one obtains the approximation

$$\Delta(e) \approx -\Theta(a(e)) \frac{a^2(e)}{4b(e)}. \tag{24}$$

The Landau expansion of the entropy surface around the equilibrium magnetization of the high-energy phase provides an explanation of the classical exponents describing the singular behaviour of the microcanonical physical quantities of the finite system. Introducing the reduced energy

$$\varepsilon := e - e_c \tag{25}$$

one can expand the functions $a(e)$ and $b(e)$ about the critical energy e_c:

$$a(e) = -A\varepsilon + a_2\varepsilon^2 + \cdots \tag{26}$$

and

$$b(e) = -B + b_1\varepsilon + b_2\varepsilon^2 + \cdots \tag{27}$$

where the constants A and B are positive. Plugging these expansions into relations (22) and (24), one gets the leading behaviour

$$m_{sp}(\varepsilon) = \pm\Theta(-\varepsilon)\sqrt{\frac{A}{B}}\sqrt{|\varepsilon|} \tag{28}$$

for the order parameter and

$$\Delta(\varepsilon) = \Theta(-\varepsilon)\frac{A^2}{4B}\varepsilon^2 \tag{29}$$

for the depth of the convex dip in the limit of small reduced energies ε. Thus the variation of the spontaneous magnetization in finite systems is described by the classical critical exponent $\tilde{\beta} = 1/2$. In addition, one can deduce the leading behaviour of the curvature of the entropy along the magnetization. For energies above the critical point, i.e. $\varepsilon > 0$, one has

$$\partial_{mm}s(\varepsilon, m_{sp}(\varepsilon)) = -A\varepsilon \tag{30}$$

and for negative reduced energies one has

$$\partial_{mm}s(\varepsilon, m_{sp}(\varepsilon)) = 2A\varepsilon. \tag{31}$$

This leads to the critical exponent $\tilde{\gamma} = 1$ characterizing the divergent susceptibility in finite microcanonical systems. Note that the slopes of the curvature $\partial_{mm}s$ at the spontaneous magnetization above and below the critical point differ by a factor 2. This is also observed in the curves obtained from the numerically calculated entropy surface (see discussion below and figure 5). From the definition (6) of the magnetic field and the expansion (17), it is apparent that the magnetic field at the critical energy e_c vanishes with an exponent $\tilde{\delta} = 3$ in the limit of small magnetizations. Similarly the critical exponent $\tilde{\alpha}$ can be shown to be 0 for both definitions of the specific heat (compare (9) and (13)).

The expansion of the entropy surface hence describes the asymptotic behaviour of the physical quantities in the vicinity of the critical point of the finite system. It has to be stressed once again that the expansion of the entropy surface is not an approximation like the Landau

expansion of the Helmholtz free energy. The Taylor expansion of the microcanonical entropy about an arbitrary point in the (e, m) space is always possible due to the analyticity of the entropy of finite systems. For the infinite system, such an expansion about the critical point cannot be performed as the thermostatic potential is singular precisely at this point. Therefore, non-trivial critical exponents can only emerge in the thermodynamic limit.

Although the physical quantities of finite microcanonical systems are always characterized by classical exponents, precursors of the non-trivial exponent of the infinite system show up if the evolution of the quantities is considered for a series of different system sizes. This evolution of the physical quantities with increasing size L can be investigated with effective critical exponents (Hüller and Pleimling 2002) or microcanonical finite size scaling relations (Kastner *et al* 2000). The microcanonical finite size scaling theory is conceptionally similar to the corresponding finite size scaling theory of the canonical ensemble.

At this stage one delicate point has to be stressed again. Whereas the Taylor expansion of the entropy can be carried out without any ambiguity for systems with continuous energies and magnetizations (e.g. xy model), this seems to be doubtful for discrete models such as the Ising model. A suitable chosen continuous function may be fitted to the data. This leads, however, to a certain degree of arbitrariness which is still related to the choice of this function. Alternatively, differentials can be replaced by (centre) differences leading to a discrete set of data points. Nevertheless, any properly chosen function will reproduce the change of the curvature along the magnetization at $m = 0$ and e_c, leading to maxima at non-zero magnetizations. It is precisely this bifurcation at e_c that gives rise to classical exponents. Different fit-functions will only lead to slightly different coefficients, the overall dependence of the expansion on e and m will be the same. The considerations in this section strictly valid only for systems with continuous e and m give a heuristic understanding of the classical behaviour of physical quantities of discrete systems.

4. Entropy surface with C_{nv} symmetry

4.1. Landau expansion of entropies with C_{nv} invariance

A general method that allows the determination of the invariant homogeneous polynomials which can appear in the Taylor expansion of the entropy is based on the concept of the complete rational basis of invariants of a group. The determination of the Landau expansion of the free energy of an infinite system with the help of the complete rational basis of invariants was first proposed by Gufan (1971) (see also Tolédano and Tolédano 1987). In this subsection this general method is applied to a microcanonical entropy surface with a C_{nv} symmetry. A prominent example of a physical system with this symmetry property of the entropy surface is the n-state vector Potts model which will be investigated in section 4.2 for a two-dimensional lattice.

An invariant homogeneous monomial of degree p with respect to a finite group can be constructed as a linear combination of products of a limited number of polynomials forming the complete rational basis of invariants. In polar coordinates $m_1 = r \cos \phi$ and $m_2 = r \sin \phi$, the complete rational basis of invariants of the finite group C_{nv} consists of the two polynomials r^2 and $r^n \cos n\phi$. The polynomial $r^2 = m_1^2 + m_2^2$ is always invariant under the modulus preserving transformations of the group C_{nv}.

The entropy of a finite microcanonical system with the symmetry

$$s(e, m_1, m_2) = s(e, C_{nv}(m_1, m_2)) \tag{32}$$

can be expanded into a Taylor series. In polar coordinates the polynomials appearing in the expansion are sums of products of the monomials of the rational basis of invariant of C_{nv}. The

basic monomials contain the angular dependence of the magnetization exclusively in the form $\cos n\phi$. Thus the entropy in polar coordinates is of the form

$$s(e, m_1, m_2) = \tilde{s}(e, r, \cos n\phi). \tag{33}$$

This form of the entropy already determines properties that are independent of the details of the Taylor expansion, e.g. the highest degree in the truncated Taylor series. These properties are solely a consequence of the symmetry of the entropy. With $b = \cos n\phi$ the equilibrium equations are

$$\frac{\partial}{\partial r} \tilde{s}(e, r, b) = 0 \tag{34}$$

for the modulus of the spontaneous magnetization and

$$\sin(n\phi) \frac{\partial}{\partial b} \tilde{s}(e, r, b) = 0 \tag{35}$$

for its angular dependence. The equilibrium condition for the angular part can be satisfied in two ways. Either the derivative $\partial_b \tilde{s}$ vanishes or $\sin n\phi$ is zero. The latter is the case for $\phi = k\pi/n$ with $k = 0, \ldots, 2n - 1$. The former way of satisfying equation (35) is discussed in section 4.3. The stability of the solution of (34) and (35) requires that the corresponding Hessian is a negative definite matrix. Suppose that the stability is guaranteed for the radial order parameter component, i.e. $\partial_{rr} \tilde{s} < 0$. At $\phi = k\pi/n$ the Hessian in polar coordinates reduces to

$$H(e, \phi = k\pi/n) = \begin{pmatrix} \frac{\partial^2}{\partial r^2} \tilde{s} & 0 \\ 0 & -\frac{n^2}{r^2} (-1)^k \frac{\partial}{\partial b} \tilde{s} \end{pmatrix} \tag{36}$$

and hence the negativity of H is satisfied if $(-1)^k \partial_b \tilde{s} > 0$. The factor $(-1)^k$ can either be $+1$ or -1 leading to maxima or saddle points of the microcanonical entropy surface at the solutions of the equilibrium conditions (34) and (35). For a positive $\partial_b \tilde{s}$ the spontaneous magnetization can have the orientations $\phi = k\pi/n$ with even k. In this situation the extrema on directions with odd k are saddle points of the entropy surface.

These considerations show that the direction of the spontaneous magnetization of an entropy with C_{nv} invariance is already determined from the symmetry properties with respect to the magnetization. The extrema of the entropy appear along the symmetry lines of the associated regular n-polygon in the magnetization plane.

To get further information about the behaviour of the entropy surface for small magnetizations, a Taylor expansion must actually be performed. The precise form of this Taylor expansion, i.e. the expansion coefficients and the degree of the truncated Taylor polynomial, determines the stability of the extrema and the form of the energy dependence of the actual order parameter $r_{sp}(e) = |m_{sp}(e)|$. To ensure the stability in the angular direction, one must have $\partial_b \tilde{s} \neq 0$ and hence the Taylor expansion has to contain at least the nth degree monomial $r^n b = r^n \cos n\phi$.

4.2. Entropy of the four-state vector Potts model

The general results of the previous subsection can be illustrated for an entropy with C_{4v} symmetry in the magnetization space. The rational basis of invariants is then given by $\{r^2, r^4 \cos 4\phi\}$ and the Taylor expansion of the entropy $s(e, r, \phi)$ up to the fourth degree term has the general form

$$s(e, r, \phi) = s_0(e) + \frac{1}{2} A(e) r^2 + \frac{1}{4} B(e) r^4 + \frac{1}{4} C(e) r^4 \cos 4\phi. \tag{37}$$

To ensure the appearance of a stable extremum for finite magnetizations, the coefficients of the fourth degree term have to satisfy $B(e) + C(e) \cos 4\phi < 0$ for all angles ϕ. The extrema of the entropy are along the symmetry directions $\phi = k\pi/4$ with $k = 0, \ldots, 7$ of the square in the two-dimensional plane. The stability in angular direction requires that the inequality

$$C(e) \cos k\pi > 0 \tag{38}$$

is satisfied. For a positive coefficient $C(e)$, this has the consequence that the maxima of the microcanonical entropy surface lie on the directions $\phi \in \{0, \pi/2, \pi, 3\pi/2\}$ provided the stability of the radial order parameter is ensured. The extrema on the four remaining symmetry directions correspond to saddle points in the entropy function.

An example of a classical spin model with C_{4v} symmetry is the vector Potts model (Wu 1982) with four states whose Hamiltonian is given by

$$\mathcal{H} = -\sum_{\langle i,j \rangle} \cos \left(\frac{\pi}{2} (k_i - k_j) \right). \tag{39}$$

The spins k_i can take the values 1, 2, 3 and 4 and be visualized by unit vectors with the orientations $0, \pi/2, \pi$ and $3\pi/2$ in a two-dimensional plane. The intensive magnetization of the system with N spins is given by

$$m_1 = \frac{1}{N} \sum_i \cos \left(\frac{\pi}{2} k_i \right) \tag{40}$$

$$m_2 = \frac{1}{N} \sum_i \sin \left(\frac{\pi}{2} k_i \right). \tag{41}$$

The system has four equivalent ground states with the spontaneous magnetizations $(1, 0)$, $(0, 1)$, $(-1, 0)$ and $(0, -1)$. These four ground state magnetizations define a square in the magnetization plane.

For a two-dimensional system with a finite number of spins, the entropy has one single maximum at zero magnetization above the critical energy e_c. Below e_c the entropy has four equivalent maxima along the directions defined by the coordinate axes. The extrema on the diagonals of the coordinate system correspond to saddle points of the entropy surface. In figure 2 the level curves of the entropy of a two-dimensional system with 64 spins are shown for two energies below the critical one. The data are calculated with the transition observable method that allows a highly efficient and accurate determination of microcanonical entropy surfaces (Hüller and Pleimling 2002). The findings show that the angular equilibrium equation (35) is satisfied by the condition $\sin 4\phi = 0$ for the four-state vector Potts model. The appearance of stable phases along the coordinate axes suggests that the coefficient $C(e)$ is indeed positive. However, it is hardly possible to obtain a reliable estimate of the fourth derivative from an entropy that has been calculated by means of Monte Carlo simulations. A direct determination of the expansion coefficients $B(e)$ and $C(e)$ is therefore not possible. To get an impression of the values of these coefficients, one can use an indirect approach. The coefficient $A(e)$ of the second degree term in the expansion (37) is determined by differentiating the entropy. The coefficients $B(e) \pm C(e)$ corresponding to the directions 0 and $\pi/2$ are then varied to achieve a good description of the data by the fourth degree expansion for small magnetizations. For the energy -0.75 near $e_c = -0.7$, this gives for the system with $L = 8$ the value -1.14 for B and the positive value 0.04 for C, in agreement with the above general considerations. For a system with $L = 10$ this procedure yields the coefficients $B = -0.804$ and the positive value 0.048 for C at energy -0.86 below the critical energy -0.806 ± 0.005. Note, however, that this procedure may lead to large errors due to the subjective assessment of
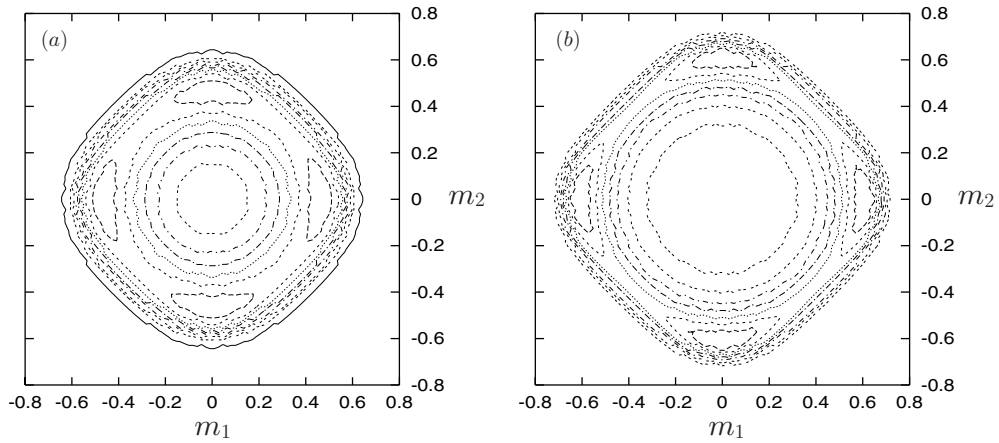
Figure 2. Level curves of the density of states of the four-state vector Potts model with 64 spins in two dimensions for the two energies -0.91 (a) and -1.06 (b) below the critical point $e_c = -0.7 \pm 0.005$. Four equivalent maxima appear along the bisectors of the square defined by the ground state magnetizations.
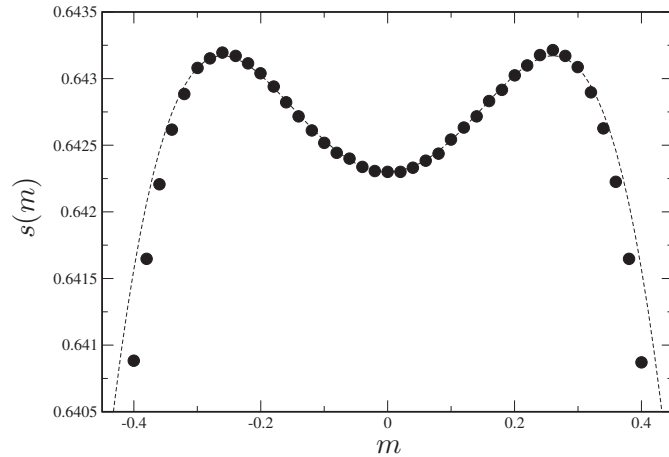

Figure 3. The entropy of the two-dimensional four-state vector Potts model with 100 spins at energy -0.86. The filled circles display the simulated data along the m_1 direction. The Taylor approximation (37) up to the fourth degree term is shown as a dashed line. The second degree coefficient 0.0257 is obtained by differentiation, and the fourth degree coefficient $\frac{1}{4}(B + C) = -0.189$ is obtained by variation. Additional higher order terms are necessary to describe the behaviour of the entropy for large magnetizations.

the agreement of the Taylor polynomial with the data for small magnetizations. The simulated entropy for the system with 100 spins together with its fourth degree Taylor approximation along the m_1 direction is displayed in figure 3.

The behaviour of the spontaneous magnetization of the two-dimensional system with 64 spins resulting from the variation of the position of the maximum is displayed in figure 4. Its energy dependence near the critical energy $e_c = -0.7$ is most suitably characterized by a square root behaviour, i.e. by the exponent $\tilde{\beta} = 1/2$. This can be understood from the general considerations in section 3. The non-zero spontaneous magnetization $m_{sp}(e)$ defines a vector
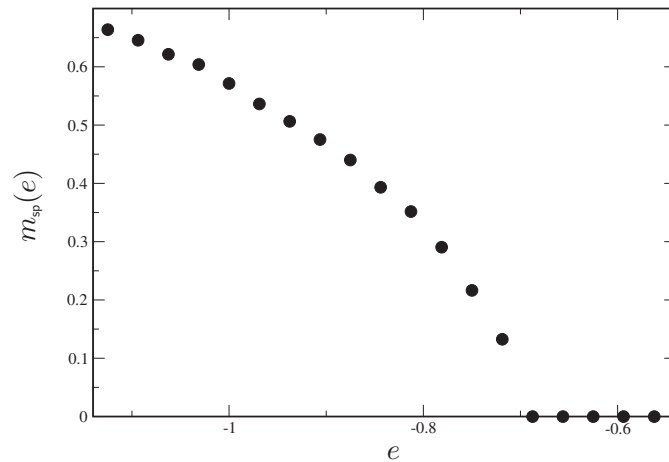
Figure 4. The spontaneous magnetization of the four-state vector Potts model with 64 spins in two dimensions as a function of energy. The data suggest a critical energy $e_c = -0.7 \pm 0.005$.
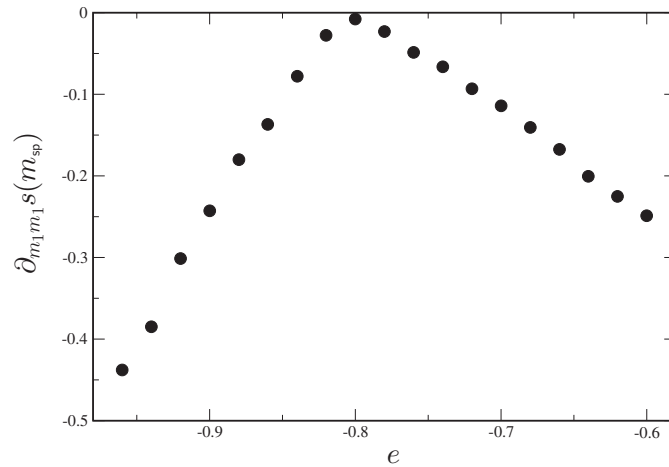

Figure 5. The (equilibrium) curvature of the entropy surface of the two-dimensional vector Potts model with 100 spins along the m_1 direction. Near the critical point $e_c = -0.806 \pm 0.005$ the curvature vanishes leading to a divergent susceptibility. At the critical point, the moduli of the gradients from the left and from the right differ by a factor 1.98, in good agreement with the prediction from the Taylor expansion.

in the order parameter space with an energy-dependent modulus $|m_{sp}(e)|$ and a fixed, energy-independent direction m_0 (compare relation (4)). Once the direction m_0 has been chosen, e.g. along the m_1 axis, the entropy depends only on the modulus $|m|$ leading to an entropy function with a one-dimensional order parameter. This function is just the cut of the entropy surface along the m_0 direction. The expansion of this function with respect to $|m|$ can be performed as in section 3 and yields the characteristic asymptotic square root energy behaviour of the microcanonical equilibrium magnetization of finite systems near the transition energy e_c. The curvature parallel to the spontaneous magnetization at the equilibrium macrostate of the system with 100 spins near the critical point is shown in figure 5. It results in a diverging
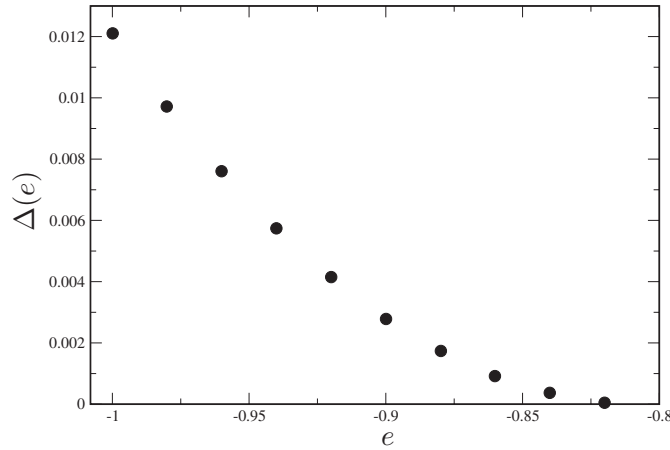
Figure 6. The depth of the convex dip of entropy surface of the two-dimensional vector Potts model with 100 spins along the m_1 direction. Near the critical point $e_c = -0.806 \pm 0.005$, the energy variation is most suitably described by a parabola.

susceptibility characterized by the critical exponent $\tilde{\gamma} = 1$. The amplitudes from the left and from the right differ approximately by a factor 2. These observations are in agreement with the general findings obtained by Taylor expanding the microcanonical entropy surface. Note, however, that the susceptibility of the four-state vector Potts model is a tensor. Due to the symmetry (32) of the entropy surface, the susceptibility tensor is diagonal with non-vanishing parallel and perpendicular components with respect to the equilibrium magnetization. The behaviour of the depth of the convex dip of the entropy surface below the critical energy e_c is shown in figure 6 for the system with 100 spins. Once again the parabolic energy dependence suggested by the above considerations is confirmed.

4.3. Energy-dependent angular magnetization

To complete the discussion of the angular equilibrium equation (35), this section focuses on the possible solution $\partial_b \tilde{s} = 0$. The derivative $\partial_b \tilde{s}$ contains the radial magnetization so that the two equilibrium equations for r_{sp} and ϕ_{sp} are coupled. This set of equations can be solved for b and gives b_{sp} or equivalently ϕ_{sp} as a function of r_{sp} and hence it will depend on the energy. Consequently, the direction of the spontaneous magnetization exhibits an energy dependence. This dependence on the energy is influenced by the precise form of the truncated Taylor expansion which determines the order parameter as a function of energy. The stability of the extremum requires additionally that the expansion must contain monomials at least up to degree $2n$. To see this consider the component $H_{\phi\phi}$ of the Hessian which is given by

$$H_{\phi\phi}^{(0)} = \frac{n^2}{r_{sp}^2}(\sin n\phi_{sp})^2 \partial_{bb}\tilde{s} \tag{42}$$

at the spontaneous magnetization. These requirements for the Taylor expansion have the further consequence that the phase diagram with respect to the expansion coefficients of the entropy allows only an isolated continuous transition (Gufan and Sakhnenko 1973).

The author does not know of any model system that exhibits an energy-dependent orientation of the microcanonically defined order parameter. Nevertheless, the general

statements of this section can be illustrated with a model entropy which is invariant under the symmetry group C_{4v}. With $b = \cos 4\phi$ and $\varepsilon = e - e_c$ the model entropy to investigate is given by

$$\tilde{s}(\varepsilon, r, b) = s_0(\varepsilon) - \frac{A}{2}\varepsilon r^2 - \frac{B}{4}r^4 + \frac{C}{4}\varepsilon^3 br^4 - \frac{G}{8}b^2 r^8 \tag{43}$$

with positive coefficients A, B and G below e_c. The coefficient C has to be non-zero. For the following discussion, it is assumed to be negative. The equilibrium equations for a non-zero spontaneous magnetization (r_{sp}, ϕ_{sp}) are

$$-A\varepsilon - Br^2 + C\varepsilon^3 br^2 - Gb^2 r^6 = 0 \tag{44}$$

and

$$\sin 4\phi (C\varepsilon^3 r^4 - Gbr^8) = 0. \tag{45}$$

The second equation (45) can be solved for b which yields

$$b = \frac{C\varepsilon^3}{Gr^4}. \tag{46}$$

At this stage it is already obvious that the direction of the magnetization vector in equilibrium will exhibit a dependence on the energy. Plugging this result into (44) gives rise to the expression

$$r_{sp} = \sqrt{\frac{A}{B}|\varepsilon|} \tag{47}$$

for the radial order parameter. In view of equation (46) one obtains

$$b_{sp} = \cos 4\phi_{sp} = \frac{CB^2}{GA^2}\varepsilon. \tag{48}$$

Inverting this result for an angle $\phi_{sp} \in [0, \pi/4]$, one ends up with the energy-dependent spontaneous direction

$$\phi_{sp}(\varepsilon) = \frac{1}{4}\arccos\left(\frac{CB^2}{GA^2}\varepsilon\right). \tag{49}$$

Note that a different interval for the angle has to be chosen for a positive coefficient C. The resulting curve $(r_{sp}(\varepsilon), \phi_{sp}(\varepsilon))$ in the two-dimensional $m_1 m_2$ plane is schematically depicted in figure 7. Only one solution for the angle of the spontaneous magnetization has been considered so far. As the entropy surface (43) is invariant under the group C_{4v}, the other solutions can be obtained by applying the transformations of C_{4v} onto the solution (r_{sp}, ϕ_{sp}) from above. This results in a star of eight possible order parameters with an energy-dependent direction. The appearance of eight solutions is related to the eight different choices of the interval of length π for the values of 4ϕ in the interval $[0, 8\pi]$ when inverting relation (48). The Hessian of the model entropy evaluated at the solution for the order parameter is diagonal. The stability of the solution requires that this Hessian has negative diagonal entries. This is indeed the case as

$$H_{rr}^{(0)} = -2A|\varepsilon| - \frac{4C^2}{G}\epsilon^6 \tag{50}$$

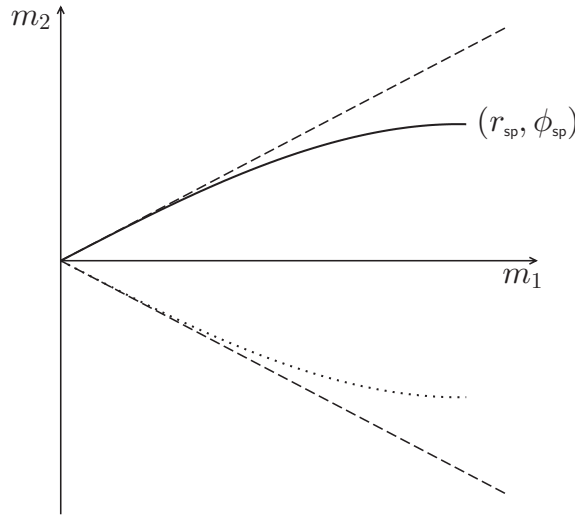**Figure 7.** Schematic behaviour of the magnetization curve (solid line) (r_{sp}, ϕ_{sp}) in the two-dimensional plane that results from the model entropy (43). The angles $-\pi/8$ and $\pi/8$ are indicated by dashed lines. A second solution (dotted line) for the order parameter is obtained by reflecting the spontaneous magnetization about the m_1 axis. Application of the rotations in C_{4v} to these two solutions gives the remaining solutions for the order parameter.

and

$$H_{\phi\phi}^{(0)} = -4(\sin 4\phi_{sp})^2 G r_{sp}^6 \tag{51}$$

are both negative.

5. Summary

The appearance of classical critical exponents in physical observables of finite microcanonical systems such as the order parameter and the susceptibility is related to the assumed analyticity of the microcanonical entropy of finite systems. This can be demonstrated by Taylor expanding the entropy function about the well-defined critical point of the finite microcanonical system. The general findings are confirmed by concrete investigations of spin systems. This suggests in turn that the assumption of an analytic microcanonical entropy function is indeed justified although a proof is still lacking. An interesting example of a classical spin system is the four-state vector Potts model with a two-component order parameter. The form of the Taylor expansion of the entropy of the four-state vector Potts model is determined by the order parameter symmetry. The general consequences of the C_{4v} symmetry on the form of the expansion of the microcanonical entropy and the resulting behaviour of the physical quantities for small magnetizations can be well verified by Monte Carlo calculations. The analyticity together with knowledge of the order parameter symmetry allows far-reaching statements about the physics of finite systems in the microcanonical ensemble.

Acknowledgments

and Michel Pleimling for stimulating discussions and helpful comments on the manuscript. The data of figure 1 was kindly supplied by Alfred Hüller.

References

Barré J, Mukamel D and Ruffo S 2001 Inequivalence of ensembles in a system with long-range interactions *Phys. Rev. Lett.* **87** 030601

Behringer H 2003 Symmetries of microcanonical entropy surfaces *J. Phys. A: Math. Gen.* **36** 8739

Binder K 1972 Statistical mechanics of finite three-dimensional Ising models *Physica* **62** 508

Creswick R J 1995 Transfer matrix for the restricted canonical and microcanonical ensembles *Phys. Rev.* E **52** 5735

Dauxois T, Holdsworth P and Ruffo S 2000 Violation of ensemble equivalence in the antiferromagnetic mean-field *XY* model *Eur. Phys. J.* B **16** 659

Gross D H E 1986a On the decay of very hot nuclei: microcanonical metropolis sampling of multifragmentation *Nuclear Fission and Heavy Ion Induced Reactions* ed W U Schröder (Harwood: Rochester) p 427

Gross D H E 1986b On the decay of highly excited nuclei into many fragments—microcanonical Monte Carlo sampling *Topical Meeting on Phase Space Approach to Nuclear Dynamics (Triest, 1985)* ed M di Toro *et al* (Singapore: World Scientific) p 251

Gross D H E 2001 *Microcanonical Thermodynamics: Phase Transitions in 'Small' Systems (Lecture Notes in Phyiscs 66)* (Singapore: World Scientific)

Gross D H E, Ecker A and Zhang X Z 1996 Microcanonical thermodynamics of first order transitions studied in the Potts model *Ann. Phys., Lpz.* **5** 446

Gufan Yu M 1971 Phase transitions characterized by a multicomponent order parameter *Sov. Phys. Solid State* **13** 175

Gufan Yu M and Sakhnenko V P 1973 Features of phase transitions associated with two- and three-component order parameters *Sov. Phys. JETP* **36** 1009

Hüller A 1994 First order phase transitions in the canonical and the microcanonical ensemble *Z. Phys.* B **93** 401

Hüller A and Pleimling M 2002 Microcanonical determination of the order parameter critical exponent *Int. J. Mod. Phys.* C **13** 947

Ispolatov I and Cohen E G D 2001 On first-order phase transitions in microcanonical and canonical non-extensive systems *Physica* A **295** 475

Kastner M 2002 Existence and order of the phase transition of the Ising model with fixed magnetization *J. Stat. Phys.* **107** 133

Kastner M, Promberger M and Hüller A 2000 Microcanonical finite-size scaling *J. Stat. Phys.* **99** 1251

Lee T D and Yang C N 1952 Statistical theory of equations of state and phase transitions: II. Lattice gas and Ising model *Phys. Rev.* **82** 410

Lewis J T, Pfister C-E and Sullivan W G 1994 The equivalence of ensembles for lattice systems: some examples and a counterexample *J. Stat. Phys.* **77** 397

Promberger M and Hüller A 1995 Microcanonical analysis of a finite three-dimensional Ising system *Z. Phys.* B **97** 341

Richer A, Pleimling M and Hüller A 2004 to be published

Stanley H E 1972 *Introduction to Phase Transitions and Critical Phenomena* (Oxford: Oxford University Press)

Tolédano J-P and Tolédano P 1987 *The Landau Theory of Phase Transitions* (Singapore: World Scientific)

Wu F Y 1982 The Potts model *Rev. Mod. Phys.* **54** 235

Yang C N and Lee T D 1952 Statistical theory of equations of state and phase transitions: I. Theory of condensation *Phys. Rev.* **87** 404