

Thermodynamic Scaling Derived via Analytic Continuation from the Classification of Ehrenfest

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Abstract

Scaling of the free energy is derived from thermodynamic arguments. The free energy is found to obey a new generalized scaling form which contains standard scaling as a special case. Contrary to standard scaling the new scaling form permits also nonuniversal exponents. The results are obtained by analytic continuation from the classification scheme of Ehrenfest.

Assuming that critical theories are scale invariant the renormalization group approach to critical phenomena allows to derive scaling hypotheses for thermodynamic functions and leads to the concept of universality [1–6]. Thus in this modern view the scaling concept derives from statistical mechanics while thermodynamically it remains a hypothesis [7, 8, 9]. It is becoming increasingly apparent however that scaling is more general than universality. This suggests to revisit traditional thermodynamics and to ask whether or not the scaling concept can be derived within it.

My objective in this paper is to derive the scaling concept within thermodynamics. From this attempt results a novel scaling form for the free energy which will be termed “thermodynamic scaling”. Thermodynamic scaling encompasses nonuniversal exponents. Methodically the results of this paper are simple consequences of analytically continuing the thermodynamic theory of phase transitions advanced by Ehrenfest [10].

Discontinuities in the derivatives of the free energy were used by Ehrenfest to distinguish and classify phase transitions [10]. Let $F(T)$ denote the free energy as a function of temperature. Assume that the system undergoes a phase transition at a critical temperature T_c . A discontinuity in the free energy itself is obviously impossible on physical grounds. Ehrenfest defines the order of the transition as the smallest integer $p \geq 1$ such that the p -th derivative of F has a discontinuity at the critical point. More formally the criterion reads

$$\lim_{T \rightarrow T_c^+} \frac{d^p F(T)}{dT^p} = A^+ \neq A^- = \lim_{T \rightarrow T_c^-} \frac{d^p F(T)}{dT^p} \quad (1)$$

where the limits A^\pm may not exist. Numerous authors have discussed the shortcomings of Ehrenfests classification [4, 11, 12]. Nevertheless if generalized to a precise definition of “order” eq. (1) becomes useful encompassing even the scaling concept.

Given the formulation (1) of Ehrenfests classification the key towards a quantitative characterization of phase transitions by their order is to rewrite (1) in terms of a finite difference quotient for an appropriate thermodynamic potential. Assuming without loss of generality that the specific heat diverges, i.e. $0 < \alpha < 1$ it is appropriate to consider the reduced entropy $S_r(T) = S(T_c)^* - S(T)$. Rewriting (1) for

this quantity reads

$$A^\pm = \lim_{T \rightarrow T_c^\pm} \lim_{N \rightarrow \infty} (\Delta T)^{-p} \sum_{j=0}^{N-1} (-1)^j \binom{p}{j} S_r(T \mp j\Delta T) \quad (2)$$

where $\Delta T = |T - T_c|/N$ and p is an arbitrary integer variable. This reformulation of eq. (1) can be analytically continued in p to give

$$A^\pm = \lim_{T \rightarrow T_c^\pm} \lim_{N \rightarrow \infty} \Gamma(-p)^{-1} (\Delta T)^{-p} \times \sum_{j=0}^{N-1} \frac{\Gamma(j-p)}{\Gamma(j+1)} S_r(T \mp j\Delta T) \quad (3)$$

where now $p \in \mathbb{R}$. As $T \rightarrow T_c$ the entropy $S_r(T \mp j\Delta T)$ can be approximated by its value for any j , in particular $j = 0$ and thus

$$A^\pm = \lim_{T \rightarrow T_c^\pm} |T - T_c|^{-p} S_r(T) \lim_{N \rightarrow \infty} N^p \times \sum_{j=0}^{N-1} \frac{\Gamma(j-p)}{\Gamma(j+1)\Gamma(-p)}. \quad (4)$$

Using

$$\sum_{j=0}^{N-1} \frac{\Gamma(j-p)}{\Gamma(j+1)\Gamma(-p)} = \frac{\Gamma(N-p)}{\Gamma(1-p)\Gamma(N)}$$

and

$$\frac{\Gamma(N-p)}{\Gamma(N)} \sim N^{-p} \quad \text{for } N \rightarrow \infty$$

yields the expected result

$$\lim_{T \rightarrow T_c^\pm} \frac{S_r(T)}{|T - T_c|^p \Gamma(1-p)} = A^\pm, \quad (5)$$

i.e., the reduced entropy becomes singular upon approach to the critical point.

Let me use this result to generalize Ehrenfests classification scheme for phase transitions. By virtue of eq. (5) there exists a unique pair (p^+, p^-) of real numbers such that $A^\pm = 0$ if $p < p^\pm$ while $A^\pm = \infty$ if $p > p^\pm$ and $0 < A^\pm < \infty$ if $p = p^\pm$. It is then natural to generalize Ehrenfests definition by defining the numbers $(p^+ + 1, p^- + 1)$ as the generalized order of a continuous phase transition. The generalized order of a transition is related to the values of the critical exponents and for the case at hand one identifies.

$$p^\pm = 2 - \alpha^\pm \quad (6)$$

where α^\pm denotes the specific heat exponents above and below T_c . In this way nonclassical values of the critical exponents follow naturally from the classification scheme of

Ehrenfest. Note that for logarithmic corrections the case $0 < A^\pm < \infty$ for $p = p^\pm$ is absent but this does not affect the order of the transition.

More generally the free energy in (1) must in general be replaced with its reduced m -th derivative where the integer m is defined as the largest integer such that $d^m F/dT^m$ is still continuous at T_c .

To obtain scaling laws it is necessary to consider more than one variable. Consider thus n reduced thermodynamic fields denoted by g_1, \dots, g_n . The critical point is now at the origin $(0, \dots, 0)$. Every approach to the critical point proceeds along a particular path which can be represented mathematically as a parametrized curve \mathcal{C} . The curve $\mathcal{C}: \mathbb{R} \rightarrow \mathbb{R}^n$ maps t into $(\gamma_1(t), \dots, \gamma_n(t))$ such that $t = 0$ corresponds to the critical point, i.e. $\gamma_i(0) = 0, i = 1, \dots, n$. The reduced m -th derivative of the free energy $F^{(m)}(g_1, \dots, g_n)$ along \mathcal{C} is a function of t alone and thus

$$\lim_{|t| \rightarrow 0} F^{(m)}(g_1(t), \dots, g_n(t)) |t|^{-p(\mathcal{C})} = A(\mathcal{C}) \Gamma(1 - p(\mathcal{C})) \quad (7)$$

where the dependence of the constants p and A on parameters other than $|t|$ has been explicitly indicated. Equation (7) represents a novel form of scaling called thermodynamic scaling.

To see this more explicitly introduce a curvilinear coordinate system in the neighbourhood of the critical point. The coordinate system is chosen such that the curve \mathcal{C} becomes the coordinate curve along the first coordinate. A possible candidate for such a curvilinear coordinate system can be defined through

$$g'_1 = \gamma_1^{-1}(g_1) \quad (8a)$$

$$g'_j = \frac{g_j}{\gamma_j(\gamma_1^{-1}(g_1))}, \quad j = 2, \dots, n. \quad (8b)$$

which assumes that γ_1 is invertible near the critical point. The curve \mathcal{C} corresponds to the coordinate curve $t \rightarrow (g'_1 = t, g'_2 = 1, \dots, g'_n = 1)$. In the new coordinate system the critical point is approached as $g'_1 \rightarrow 0$. Considering again the reduced m -th derivative of the free energy as a function of the first coordinate gives

$$\begin{aligned} \lim_{g'_1 \rightarrow 0} F^{(m)}(g'_1, \dots, g'_n) g_1^{-p(g'_2, \dots, g'_n)} \\ = A(g'_2, \dots, g'_n) \Gamma(1 - p(g'_2, \dots, g'_n)) \end{aligned} \quad (9)$$

This way of rewriting eq. (7) emphasizes the parametric dependence of the constants p and A on the $n - 1$ variables of eq. (8b) and the power law dependence on the distance to the critical point.

Standard scaling can be recovered from eq. (9). The requirement $\gamma_i(0) = 0, i = 1, \dots, n$ is fulfilled if to leading order $\gamma_i(t) = c_i t^{a_i}$ near the critical point with $c_i, a_i \in \mathbb{R}$ constant. Note however that other forms for $\gamma_i(t)$ are also consistent with thermodynamic scaling. For the case $n = 2$ one has

explicitly $g'_1 = t = \gamma_1^{-1}(g_1) = (g_1/c_1)^{1/a_1}$ and $g'_2 = (c_1^{a_2/a_1}/c_2)(g_2/g_1^{a_2/a_1})$. Then eq. (9) leads to

$$F_s^{(m)}(g_1, g_2) = g_1^{q(g_2/g_1^{a_2/a_1})} Y\left(\frac{g_2}{g_1^{a_2/a_1}}\right) \quad (10)$$

for the singular part of m -th reduced derivative of the free energy. This shows that in general there are two scaling functions $q(x)$ and $Y(x)$, one for the exponent and one for the amplitude. Standard scaling is recovered if $q(x)$ is constant.

Summarizing, this paper has shown that continuous phase transitions can be usefully classified according to their generalized noninteger orders. The classification implies a new form of thermodynamic scaling. Because the classification is a purely mathematical consequence of thermodynamics it furnishes a simple and general derivation of scaling within thermodynamics. Thermodynamic scaling is more general than standard scaling and allows for violations of universality because critical exponents may become scale dependent.

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