Second-order phase transitions in systems with a finite number of particles

A. L. Tseskis

Scientific Research Institute of the Canning and Vegetable-Drying Industry, Russian Academy of Agricultural Sciences, 142700 Vidnoe, Moscow Region, Russia

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The two-dimensional Ising model is used to calculate the dependence, at the transition point, of the thermodynamic potential on the number of particles for the case where the latter is finite. The potential, together with all its derivatives, is found to be continuous but is not additive. The results obtained are shown to be related to the critical exponent and the effective Hamiltonian of the continuous model. © *1994 American Institute of Physics.*

A second-order phase transition (and any phase transition in general) is sometimes said to be possible only in unbounded systems.[1,2] The partition function and the related quantities are regarded as a result of the transition to the thermodynamic limit $V \to \infty$ ($N/V=\text{const}$). On the other hand, the more physical case involving a finite number of particles is the one realized in practice. In this situation, however, thermodynamic functions must have no singularities at any finite temperature.[2] True singularities must therefore manifest themselves in the transition to the limit $N \to \infty$. Thus, near the transition temperature[1)] the thermodynamic potential of a system with a finite number of particles N must have a component as a function of the number of particles and temperature (which depends parametrically on N) that is regular for N finite but has a singularity at the transition point as $N \to \infty$. We will establish the form of this function for the two-dimensional Ising model and will attempt to generalize the result obtained.

Clearly, this cannot be a linear function. Hence, we can assert that in a system with a finite number of particles involved in a second-order phase transition the thermodynamic quantities are not additive. The physics of this rests in the fact that near the transition temperature the fluctuations are large, so that small parts of the system[3] are not statistically independent.[4] For instance, the mean square of the fluctuations of an "additive" quantity f, that is, $\langle(\Delta f)^2\rangle$, is determined not only by the N terms of the sum $\Sigma_{i=1}^{N}\langle(\Delta f_i)^2\rangle$ but also, generally speaking, by nonzero terms $\langle\Delta f_i \Delta f_k\rangle_{i\neq k}$. If the correlation radius proves to be of the order of the system size, we have $\langle(\Delta f)^2 \sim N^{1+\varepsilon}\rangle$ ($\varepsilon>0$), and the contribution of fluctuations to the thermodynamic quantities becomes nonadditive.

We now carry out direct calculations for the Ising model by using Onsager's solution following Ref. 5 (see also Ref. 2). It is immediately clear that for finite values of N the thermodynamic quantities in the Ising model can have no singularities since the partition function is reduced here to a finite (but large) number of terms that are continuous with all their derivatives (in this connection see the statements concerning a lattice which is infinite in the direction parallel to one of its axes[6–8]). We now examine the partition function of a square lattice ($n^2=N$). Its calculation reduces[2] to finding the quantity

$$\Lambda=\exp\left[\tfrac{1}{2}(\gamma_1+\gamma_3+\cdots+\gamma_{2n-1})\right], \tag{1}$$

where the γ_k are the positive solutions of the equations ($k=1,3,\ldots,2n-1$)

$$\cosh \gamma_k=\cosh 2\varphi \coth 2\varphi-\cos\frac{\pi k}{n}, \quad \varphi=\frac{J}{T}, \tag{2}$$

where J is the spin–spin coupling constant, and T the temperature. It is found that $\gamma_1<\gamma_3<\ldots<\gamma_{2n-1}$. The usual way to write the sum in the parentheses in Eq. (1) is

$$\lim_{n\to\infty}\sum_{k=1}^{n}\gamma_{2k-1}=\frac{n}{2\pi}\int_0^{2\pi}\gamma(\alpha)\,d\alpha \quad \left(\frac{\pi}{n}(2k-1)\Rightarrow\alpha\right) \tag{3}$$

or, since Eqs. (2) imply $\gamma(\alpha)=\gamma(2\pi-\alpha)$,

$$\lim_{n\to\infty}\sum_{k=1}^{n}\gamma_{2k-1}=\frac{n}{\pi}\int_0^{\pi}\gamma(\alpha)\,d\alpha. \tag{4}$$

Under such a transition the singularity in the thermodynamic functions (at $n=\infty$) originates in the lower limit of integration in (4). But for n finite instead of (3) we have (from the Euler–Maclaurin formula)

$$\sum_{k=1}^{n}\gamma_{2k-1}=\frac{n}{2\pi}\int_\delta^{2\pi-\delta}\gamma(\alpha)\,d\alpha, \quad \delta=\frac{\pi}{n}, \tag{5}$$

since the first and last terms in the sum are, respectively, $\gamma_1\equiv\gamma(\pi/n)$ and $\gamma_{2k-1}\equiv\gamma(\pi(2k-1)/n)$. That we can apply the Euler–Maclaurin formula follows directly from the fact that all the derivatives of the functions $\gamma(\alpha)$ exist and are continuous for $0<\alpha<2\pi$, while the terms left out and denoted by three dots,

$$-\frac{1}{2}\left[\gamma\left(\frac{\pi}{n}\right)-\gamma\left(2\pi-\frac{\pi}{n}\right)\right]$$

and

$$(-1)^k\frac{B_k}{(2k)!}\left(\frac{\pi}{n}\right)^{2k-1}\left[\gamma^{(2k-1)}\left(\frac{\pi}{n}\right)-\gamma^{(2k-1)}\left(2\pi-\frac{\pi}{n}\right)\right],$$

$$k=1,2,\ldots$$

(the B_k are Bernoulli numbers), vanish in view of (2). As for the form of the Euler–Maclaurin formula proper in this case (without the remainder term), it is justified by the fact that all the even-order derivatives of the function $\gamma(\alpha)$ are of the same sign.[9] Indeed, for the most "risky" value $\cosh 2\varphi \coth 2\varphi=1$ Eq. (2) yields

$$\gamma'(\alpha)=\frac{\sin\alpha}{\gamma(\alpha)}=\frac{\sin\alpha}{1-\cos\alpha}=\cot\frac{\alpha}{2}.$$

If we now recall the well-known expansion

$$\cot x=\frac{1}{x}-\frac{x}{3}-\cdots-\frac{2^{2n}B_n}{(2n)!}x^{2n-1}-\cdots,$$

we can easily see that all the even-order derivatives of $\gamma(\alpha)$ for small values of α are negative.

Thus, for n finite Eq. (3) implies

$$\sum_{k=1}^{n}\gamma_{2k-1}=\frac{n}{2\pi}\int_{\delta}^{2\pi-\delta}\gamma(\alpha)\,d\alpha=\frac{n}{\pi}\int_{\delta}^{\pi}\gamma(\alpha)\,d\alpha, \tag{6}$$

where

$$\cosh\gamma(\alpha)=\cosh 2\varphi\coth 2\varphi-\cos\alpha.$$

Next, as is common practice, we use the well-known representation

$$|\gamma|=\frac{1}{\pi}\int_0^{\pi}d\alpha'\,\ln(2\cosh\gamma-2\cos\alpha')$$

and, proceeding with the calculation of the thermodynamic potential, we arrive at the following expression for its singular part:

$$F_{\text{sing}}=-\frac{NT}{2\pi^2}\int_{\delta}^{\pi}d\alpha\int_0^{\pi}d\alpha'\,\ln(\cosh 2\varphi\coth 2\varphi -\cos\alpha'-\cos\alpha). \tag{7}$$

As with the zero lower limit in the inner integral in (7), we must assume that the phase transition occurs when the argument of the logarithm is at its minimum; because the lower limit of integration is δ this minimum is now nonzero and equal to $\frac{1}{2}\delta^2$ for small values of δ (to within the sum of the terms of the next even orders). Thus, expanding the argument of the logarithm in (7) near the minimum in a series of powers of $t=T-T_c$, α, and α', we obtain

$$F_{\text{sing}}=-\frac{NT}{2\pi^2}\int_{\delta}^{\pi}d\alpha\int_0^{\pi}d\alpha'\,\ln\left[ct^2+(\alpha+\delta)^2-\delta^2+\frac{\alpha'^2}{2}\right], \tag{8}$$

where c is a constant. Integrating in (8), we arrive at the final expression for F_{sing} in the form (a and b are constants)

$$F_{\text{sing}}=aN+bN\left(ct^2+\frac{3\pi^2}{N}\right)\ln\left(ct^2+\frac{3\pi^2}{N}\right). \tag{9}$$

From (9) it follows that the singular part of the potential is not additive, is continuous along with all its derivatives (as it should be), and assumes the conventional form as $N\to\infty$. It can also be seen that the very form of the argument of the logarithm in (9) immediately relates this result to the theory based on critical exponents. Indeed, bearing in mind that $N\sim L^2$ (here L is the linear size of the system) and the fact that as $t\to 0$ and $r_c\to\infty$ we can assume that $r_c\sim L$, for a certain value of z we can write the following:

$$\begin{aligned}&(t^2)^z\propto t^{-\nu}, \quad L\to\infty,\quad t\neq 0,\\ &(L^{-2})^z\propto L,\quad L\neq\infty,\quad t\to 0,\end{aligned} \tag{10}$$

so that by excluding z we immediately get $\nu=1$, as expected. We could have also used Eq. (9) directly to find the scaling size Δ_t (Ref. 3) from the condition that both terms in the argument of the logarithm get multiplied by the same number under the scaling transformation $r\to r/u$. This yields $\Delta_t=1$, that is, again $\nu=1$.

Returning to Eq. (9), we note that the dependence on the number of particles contained in it could be obtained much more simply if we were to use the method of solution of the two-dimensional Ising model employed by Vdovichenko[10] (see also Ref. 3). According to that solution, the expression for the thermodynamic potential incorporates the following quantity as a separate term (here $x=\tanh(J/T)$):

$$\sum_{p,q=0}^{n}\ln\left[(1+x^2)-2x(1-x^2)\left(\cos\frac{2\pi p}{n}+\cos\frac{2\pi q}{n}\right)\right],$$

$$x=\text{th}\,\frac{j}{T}$$

so that for n finite in passing to integration the variables $p,q=0$, 2π should be excluded because the spins at the edges of the lattice are not of the same status as the other spins. In this case, however, the result could be considered only as a not-too-rigorous estimate because the boundary effects are ignored, which is characteristic of the given method.[2)] It can easily be verified that in such a calculation the critical temperature (which corresponds, as it did earlier, to the minimum of the argument of the logarithm) is shifted to the left relative to T_c ($N=\infty$) by a quantity of order $1/N$ (assuming, obviously, its usual value for $N\to\infty$). The first to notice the presence of this shift were Fisher and Ferdinand,[11] who in order to estimate it also did calculations that ignored lattice edges.

Finite-size effects in connection with critical behavior in thin films have been discovered both theoretically[12,13] and experimentally.[14,15] The main result is reduced to the statement about the finiteness of specific heat at the transition point (thanks to the small thickness of films this statement can be verified directly by experiments).

More important, however, is the fact (briefly noted above) that the very form of Eq. (9) allows for certain general assumptions about critical phenomena in general and about relations linking critical exponents in particular. Indeed, we can assume that in a system with the effective Hamiltonian (not necessarily one-parameter) $H(\eta;a,b,...,T)$ a phase transition corresponds to a certain "summation" with a function $F\{G(a,b,...,T)+K(V)\}$ possessing the following properties: it has a singularity when the argument is zero, the function G is regular, and $K(V)$, as in Eq. (9), has the form $K\propto L^{-\Delta}$ (here, generally, it is not required that Δ be equal to d). Then the transition temperature is such that at $T=T_c$ the function G has a minimum equal to zero (it is specifically to find such values of the parameters, a^*, b^*, etc., at which this is possible that the method of the renormalization group is used, as is done in Ref. 16 for the s^4-model). The expansion of G in a series near the minimum must not contain odd powers of t, since otherwise the argument of F vanishes even for finite dimensions of the system. Thus, we must expect all the respective physical quantities near $T=T_c$ to have the form

$$\mathscr{F}\equiv\mathscr{F}(t^2+L^{-\Delta}). \tag{11}$$

It is now clear that Eq. (11) is not only a means for finding the scaling sizes but also a source for obtaining the well-known relations linking the critical exponents. Indeed, bearing in mind the power-like nature of the singularities of physical quantities near the transition temperature, we obtain from Eq. (11) and, say, the fact that $\langle\eta\rangle\sim t^\beta$ the following:

$$\Delta_t=\frac{\Delta}{2}, \quad \Delta_\eta=\frac{\beta\Delta}{2}. \tag{12}$$

Similarly, assuming that the dependence on an external field at $t=0$ of the respective quantities is also given by an expression of the form (11) with h instead of t and with, obviously, another value of Δ, say Δ', we can easily (allowing for the fact that $r_c\sim h^{-\mu}$ holds in the case of "strong" fields) arrive at the equation

$$\Delta_h=\frac{\Delta'}{2}. \tag{13}$$

Now, since for small values of t and h we can assume that $r_c\sim L$, we have

$$\Delta=\frac{2}{\nu}, \quad \Delta'=\frac{2}{\mu},$$

which immediately results in the well-known relations

$$\Delta_t=\frac{1}{\nu}, \quad \Delta_\eta=\frac{\beta}{\nu}, \quad \Delta_h=\frac{1}{\mu}.$$

It is important to note that these relations, as well as those obtained below that incorporate critical exponents, are entirely independent of the exponents in (11) and in the similar formulas for the field h.

Moreover, since this approach makes it possible to express the dependence of C, $\langle\eta\rangle$, etc. on the size of the system, it must also yield the finite-size scaling relations.[12,17] Indeed, for, say, $\langle\eta\rangle$ we have

$$\langle\eta\rangle=t^\beta(L\to\infty) \underset{t=0}{\Rightarrow} \langle\eta\rangle\sim L^{-\beta/\nu}. \tag{14}$$

If we now take the susceptibility of the system,

$$\chi\sim t^{-\gamma}(L\to\infty) \underset{t=0}{\Rightarrow} \chi\sim L^{\gamma/\nu}, \tag{15}$$

and allow for the fact that $\langle\eta\rangle L^d$ and $\chi^{1/2}L^{d/2}$ have the same scaling size,[4] from (14) and (15) we obtain

$$d-\frac{\beta}{\nu}=\frac{\gamma}{2\nu}+\frac{d}{2}$$

or, bearing in mind that $\alpha+2\beta+\gamma=2$, we have

$$d\nu=2-\alpha,$$

the well-known relation of scaling invariance.

The formula

$$|M|=\langle\eta\rangle L^d\sim L^D, \quad D=d-\frac{\beta}{\nu}$$

for the Ising model determines how the total magnetization of a system depends on the system size at $t=0$. Since D is smaller than d and is not an integer, it is customary to speak of what has become known as fractal dimension[17] and link it with certain geometric properties in the distribution of the order parameter (see also Ref. 18). Determining this quantity actually gives one more relation linking critical exponents. If, in addition, both exponents in (11) were known, we could find all the critical exponents in general. A numerical experiment to determine D is described in Ref. 19. For $d=2$ it appears that $D=1.875$, in complete accordance with the known values of the exponents. For $d=3$ it appears that $D\approx2.46$. If for this case we put $\Delta=d$ in (11), we immediately find that $\nu=2/3$ and $\alpha=0$. For the other exponents we have the following: $\beta=0.36$, $\gamma=1.28$, $\delta=4.56$, $\varepsilon=0$, $\mu=0.41$, and $\zeta=0.08$.

We also note that the exponent Δ in (11) is probably close to d. Indeed, if addition to this assumption we assume that $r_c\propto t^{-\nu}$, we immediately get $\nu=d/2$, which agrees with the well-known theoretical and experimental results not only for $d=2$ and $d=3$ but also for $\nu=1/2$ when $d=4$ (see Refs. 16 and 20).

Another fact worth noting is that obtaining the above results, say (15), by employing expressions of the form (11) may be preferable to employing standard finite-size scaling expressions, which are used in conducting many computer experiments for various discrete models; see Refs 21 and 22 (the Ising model; see also the many sources cited in Ref. 21) and Ref. 23 (the Gross–Neveu and Higgs–Yukawa models). For one thing, the common expression for susceptibility is

$$\chi=L^{\gamma/\nu}g(L^{1/\nu}t),$$

where $g(x)$ is a universal function whose argument is chosen, obviously, from the requirement that its scaling size vanish (of course, $g(x)$ is regular in the neighborhood of $x=0$). Typically, however, it is extremely difficult to select a similar expression for the free energy, which, in addition, would agree with the exact solution of the two-dimensional Ising model. Privman[24] took the expression for the free energy per unit volume from Refs. 11 and 12 and modified it in the following manner:

$$f=\psi_0(t)+\frac{\psi_1(t)}{L}+\dots+\frac{\psi_d(t)}{L^d},$$

$$\psi_0\propto|t|^{\nu d}, \quad \psi_1\propto|t|^{\nu(d-1)}, \quad \psi_d\propto \ln t.$$

Clearly, this expression cannot be considered satisfactory because then f is not regular at finite values of L, which is impossible. (Fisher and Barber[12] were the first to point out the need to include additional terms to remove the singularities in expressions of this type for finite values of L.) Hence, the merits of using expressions of the form (11) to describe finite-size effects, expressions that also correspond to the exact solution of the two-dimensional Ising model, appear obvious.

The latter is also stressed by the following important fact. The Gaussian model with the Hamiltonian[3]

$$H=\int [\alpha t \eta^2+g(\nabla \eta)^2]\,dV$$

leads, as is known, to a true singularity in the thermodynamic quantities even for a system with finite V; the trivial dependence of the quantities on the volume here is a consequence of the homogeneity of the Hamiltonian density in η. On the other hand, the model with the effective Landau Hamiltonian

$$H_{\text{eff}}=\int [\alpha t \eta^2+b\eta^4+g(\nabla \eta)^2]\,dV$$

exhibits no such homogeneity. Since for positive values of b the corresponding functional integral is finite (in the Gaussian model the infinity appears as a result of summing over the variable η at $t=0$ and $k=0$), the singularity should appear not as pronounced when the dimensions of the system are finite. After we pass to the Fourier transform η_k and replace $\eta_k V^{1/2}$ with η_k (this last transformation results in the appearance in the expressions for the thermodynamic quantities of an inessential volume-dependent additive term), the coefficient of the fourth-order terms is found to be equal to b/V, so that all corrections caused by such terms are reduced to a series expansion in powers of $1/V$ (and, of course, are also functions of t). It seems quite plausible that the result of such calculations will closely resemble (11). This is also a direct indication of the merits of describing a critical singularity by employing the effective Landau Hamiltonian (in this approach at least the presence of a transition is obvious) in comparison to Wilson's approach, in which the Hamiltonian density contains the term $a\eta^2$ with $a \neq 0$ and the very existence of T_c is a corollary of the fixed-point hypothesis and other far-reaching assumptions. The results of the present work show that here, too, the calculations of the type done in Ref. 16 must be modified by considering relations containing the finite size of the system explicitly.

[1)]This, of course, requires that the very idea of a phase transition for N finite and the respective temperature T_c be defined.

[2)]In this sense, the initial solution of Onsager is exact under the "toroidal" boundary condition inherent in it.

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