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Scaling hypothesis and nonzero-field critical invariants

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Assuming the static scaling hypothesis, a proof is given for the existence of invariants (Q) associated with the extrema of the thermodynamic functions: nonzero-field susceptibility, nonzero-field specific heat, nonzero-wave-vector correlation function. In the framework of the Landau theory, the value of the invariant Q related to the susceptibility is found to be $Q=2$. Experimental measurements of the maxima of the nonzero-electric-field susceptibility for a ferroelectric triglycine sulfate TGS crystal give a value 1.87 ± 0.05 for the invariant Q. This result provides new evidence of a deviation from Landau theory in the thermodynamic behavior of the TGS crystal.

INTRODUCTION

All the data on the critical behavior of a physical system give a scaling function, and each point of the scaling function is a critical invariant. Despite the fact that this function has been determined experimentally in many cases (see experimental works cited in Refs. 1–3), to the best of our knowledge there is no theoretical derivation of this function based on exact model calculations in a nonzero (electric, magnetic, reduced pressure, etc.) field E. There do exist, however, precise and/or almost precise (series expansions plus extrapolations by Padé approximants and the renormalization-group method) results relating to two particular points of the scaling function ($\tau\neq0$, $E=0$) and ($\tau=0$, $E\neq0$), where $\tau=T/T_c-1$. With these points are associated the invariants: (a) critical indices $\alpha,\beta,\gamma,\delta,\nu,\eta$, and (b) combinations A_0^+/A_0^-, Γ_0^+/Γ_0^-, $R_x=\Gamma_0^+DB^{\delta-1}$, $R_c=A_0^+B^{-2}\Gamma_0^+$, etc., of critical amplitudes of specific heat $A_0^{\pm}$, susceptibility $\Gamma_0^{\pm}$, order parameter (P, polarization, magnetization, reduced pressure, etc.), and B and D ($P=B\tau^{\beta}$, $E=DP^{\delta}$ at $\tau=0$). The superscript $+$ ($-$) indicates that the given magnitude is determined only for $\tau>0$ ($\tau<0$).

There are also known invariants associated with nontrivial points ($\tau\neq0$, $E\neq0$) of the scaling function: the gap exponent Δ and the Watson invariants. However, the determination of these invariants from experimental data is a difficult and not particularly accurate process, since it requires the investigation of field derivatives of the Gibbs potential of higher order than the second. We propose the study of another invariant Q associated with a nontrivial point ($\tau\neq0$, $E\neq0$) of the scaling function. The invariant Q may be defined by the equation

$$Q=\chi(\tau_m,0)/\chi(\tau_m,E)\ ,$$

where $\tau_m=T_m/T_c-1$, and $T_m(E)$ is the temperature at which the susceptibility $\chi(\tau,E)$ takes maximum (and/or minimum) values for the given value of field E. Despite the fact that in the definition of Q we have $\tau_m=T_m/T_c-1$, a knowledge of T_c is not necessary to determine this invariant. This makes possible an easier experimental verification of the theory. Instead of studying this invariant at the maximum it may be considered, for instance, at the point of inflection of the susceptibility curve. The advantage of the maximum over all the other susceptibility points is that the maximum may be most accurately measured. The maximum (or minimum) also has another feature distinguishing it from all other points of the susceptibility curve; i.e., only at this point does the scaling function satisfy Eq. (2a).

The invariant Q is associated with the vanishing of the third-order derivative of the Gibbs potential $\partial^3G(\tau,E)/\partial E^2\partial\tau=0$ for $\tau\neq0$ and $E\neq0$, whereas the other invariants mentioned here are related to the behavior of corresponding thermodynamic functions, i.e., first- and second-order derivatives of the Gibbs potential $G(\tau,E)$ for $\tau\neq0$ and $E=0$ or for $\tau=0$ and $E\neq0$, respectively.

In the theoretical part we show that if a physical system behaves according to the scaling hypothesis then the susceptibility (and other functions) may exhibit for $|\tau|\neq0$, in a given phase, the extrema and associated with each of them two nonuniversal (2b), (2e) and one universal (2f) constant. These predictions are confirmed in the experimental part for a triglycine sulfate (TGS) crystal.

THEORY

Assuming the static scaling hypothesis[1–3] the susceptibility $\chi^{\pm}(\tau,E)$ may be written in the universal form:

$$\chi^{\pm}(\tau,E)/\chi_0^{\pm}=f_{\pm}(y)\geq0,\quad \chi_0^{\pm}=\Gamma_0^{\pm}|\tau|^{-\gamma}\ , \tag{1a}$$

$$y=E\chi_0^{\pm a},\quad a=\Delta/\gamma=\delta/(\delta-1)>0\ , \tag{1b}$$

where the functions R^+ and R^- ($R=\chi,\Gamma$) are restricted to the high temperatures ($T>T_c$) and low temperatures ($T<T_c$), respectively, $f_{\pm}(y)$ are the corresponding scaling functions above (f_+) and below (f_-), the critical point. Taking the derivative of $\chi^{\pm}(\tau,E)$ with respect to τ equal to zero, $\chi^{\pm\prime}=\partial\chi^{\pm}(\tau,E)/\partial\tau=0$, from Eqs. (1) we may obtain the condition

$$f_{\pm}(y)+ya\dot{f}_{\pm}(y)=0,\quad 0\leq y<\infty\ , \tag{2a}$$

for the extreme point y, where $\dot{f}_{\pm}=df_{\pm}(y)/dy$. Equation (2a) is algebraic with respect to variable y and differential with respect to the function f. In the general case of function f, the algebraic equation (2a) for y can exhibit only discrete solutions (y_i), which are responsible for the susceptibility extrema (maxima and minima). Thus we obtain the first constant y_i

$$y_i = E\chi_0^{\pm a}(\tau_i) = \Gamma_0^{\pm a} E|\tau_i|^{-\Delta} = \text{const} \tag{2b}$$

at each ith extremum of susceptibility, where $\tau_i = T_i/T_c - 1$ is the temperature at which nonzero-field susceptibility exhibits the ith extremum for a given value of E. Equation (2b) gives the power-law behavior

$$E = (y_i/\Gamma_0^{\pm a})|\tau_i|^{\Delta} \tag{2c}$$

of the field E versus $|\tau_i|$ of the ith extremum of $\chi^{\pm}(\tau,E)$ at $\tau=\tau_i$. On the other hand, the formal solution of the differential equation (2a) for scaling function f is given by

$$f_{\pm}(y) = A/y^{1/a}, \quad A = \text{const} \geq 0 , \tag{2d}$$

where A is some non-negative integration constant. Inserting the solutions (y_i) of the algebraic equation (2a) into Eq. (2d) we can determine the second constant A separately at each extremum of susceptibility

$$A_i = A(y_i) = f_{\pm}(y_i) y_i^{1/a} = E^{1/a}\chi^{\pm}(\tau_i,E) = \text{const} , \tag{2e}$$

where use has been made of Eqs. (2d), (1a), (1b), and (2b).

The constants (2b) and (2e) are not given in dimensionless units, i.e., they are not universal constants as are critical exponents. But we can combine them to form the invariant Q_i where

$$Q_i = y_i^{1/a}/A_i = \chi_0^{\pm a}(\tau_i)/\chi^{\pm}(\tau_i,E)1/f_{\pm}(y_i) = \text{const} , \tag{2f}$$

relating the quotient of the initial susceptibility $\chi_0^{\pm}(\tau)$ and nonzero-field susceptibility $\chi^{\pm}(\tau,E)$ at $\tau=\tau_i(E)$ for various values of E, due to Eq. (2c). The quotient (2f) takes a numerical value and is a constant for different physical systems belonging to the same universality class. We now show that τ_i and Q_i are well defined for discrete solutions $y=y_i$ of Eq. (2a). The proof follows simply: if $y=y_i$ is not discrete but continuous in some range $y_1 < y < y_2$, then from Eqs. (2a) and (2d) it is clear that $\chi(\tau,E) = A/E^{1/a}$ (independent of τ) for

$$(E\Gamma_0^{\pm a}/y_2)^{1/\Delta} \leq \tau \leq (E\Gamma_0^{\pm a}/y_1)^{1/\Delta} \quad \text{and } \tau_i$$

would not be well defined.

Equations (2d) and (2e) allow us to state that the value of the scaling function $f_{\pm}(y)$ is equal to the value of the function $A_i/y^{1/a}$ at the extreme point y_i and that these functions take different values at all other points $y \neq y_i$. We now show that any nonzero solution $0 < y_i < \infty$ of Eq. (2a) is the double root of the equation $S(y)=0$, where $S(y)$ is the difference

$$S(y) = A_i/y^{1/a} - f_{\pm}(y) \tag{3}$$

of the function $A_i/y^{1/a}$ and the scaling function $f_{\pm}(y)$ and A_i is defined in Eq. (2e). The above statement is supported by the following arguments: y_i has to satisfy simultaneously Eqs. (1a), (1b), (2a), (2d), and (2e); where $A_i > 0$, the temperature derivative of susceptibility $\chi^{\pm}(\tau,E)$ has to vanish, i.e., $\partial\chi^{\pm}(\tau,E)/\partial\tau = 0$. These facts imply that the second-order derivative ($\chi^{\pm''}$) of $\chi^{\pm}(\tau,E)$ with respect to τ is proportional to $\ddot{S}(y_i)$, as follows:

$$\partial^2\chi^{\pm}(\tau,E)/\partial\tau^2 = -\ddot{S}(y_i)(ay_i\chi_0^{\pm'}/\chi_0^{\pm})^2\chi_0^{\pm} , \tag{4}$$

where

$$\ddot{S}(y_i) = -[a^2 y_i^2 \ddot{f}_{\pm}(y_i) - (a+1)A_i/y_i^{1/a}](ay_i)^{-2} \tag{5a}$$

and

$$S(y_i) = \dot{S}(y_i) = 0 . \tag{5b}$$

Therefore the Taylor expansion of $S(y)$ at $y=y_i$ to the second order is given by

$$S(y) = \tfrac{1}{2}\ddot{S}(y_i)(y-y_i)^2 , \tag{6}$$

i.e., y_i is a double root of the equation $S(y)=0$. From these considerations a conclusion can be formulated: any simple (and, in general, not double) root (y_r) of the equation $S(y_r)=0$ [cf. Eq. (3)] cannot be a solution of Eq. (2a) and therefore does not give the extrema of susceptibility.

It may be seen from Eqs. (4) and (1) that

$$\chi^{\pm''} = -\Gamma_0^{\pm}(\Delta y_i)^2\ddot{S}(y_i)|\tau_i|^{-(2+\gamma)} .$$

From this fact and Eqs. (2b), (2c), and (2e) it follows that when E increases, $|\tau_i|$ increases, $\chi^{\pm}(\tau_i,E)$ decreases, and the peak of maximum or the valley of minimum of susceptibility becomes increasingly broad. This behavior of the maxima cannot be interpreted as the E-T line of critical points.

We now prove that the smallest nonzero solution (y_1) of Eq. (2a) gives the maximum of susceptibility. This can be shown as follows. From Eqs. (1a) and (1b) it may be seen that $f_{\pm}(0)=1$; from Eq. (3) we may conclude that $S(y)>0$, for all $y<y_1$. This implies that, according to Eq. (6), $\ddot{S}(y_1)>0$. Then from Eq. (4) we know that $\chi^{\pm''}<0$. Hence we have that if y_1 is the smallest nonzero solution of Eq. (2a) it gives the maximum of susceptibility $\chi^{\pm}(\tau,E)$ for fixed values of E when τ is varied around $\tau=\tau_1$. We are now able to draw several conclusions from the discussion above. If there are more solutions, $y_1<y_2<y_3\cdots$, of Eq. (2a), then odd ones (y_{2i+1}) correspond to maxima and even ones (y_{2i}) to minima of susceptibility. If there exists only one nonzero solution (y_1) of Eq. (2a) it always leads to a maximum of susceptibility. If some of the solutions of Eq. (2a) coincide with zero ($y=0$) then according to Eqs. (1a), (1b), and (2e), $f_{\pm}(0)=1$ and the integration constant $A=0$. Therefore there are no extrema of susceptibility in this case.

We are now in a position to formulate the thesis: If the nonzero-field susceptibility $\chi^{\pm}(\tau,E)$ takes the form (1a), (1b) (i.e., when the static scaling hypothesis is true), then nonzero solutions ($y_i>0$) of the algebraic equation (2a) determine the invariants $Q_i(2f)$ associated with the extrema of $\chi^{\pm}(\tau,E)$. This thesis can be applied also to the nonzero-field specific heat $C^{\pm}(\tau,E)$ and to nonzero-wave-vector correlation function $\chi^{\pm}(\tau,\mathbf{q})$ ($\mathbf{q}$, wave vector) because, according to the static scaling hypothesis,[1-3] these functions can be represented by the equations

$$C^{\pm}(\tau,E)/C_0^{\pm}=g_{\pm}(y)\geq 0,\quad C_0^{\pm}=A_0^{\pm}|\tau|^{-\alpha}\ , \tag{7a}$$

$$y=EC_0^{\pm a},\quad a=\Delta/\alpha,\quad \alpha\neq 0\ , \tag{7b}$$

and

$$\chi^{\pm}(\tau,\mathbf{q})/\chi_0^{\pm}=h_{\pm}(y)\geq 0\ , \tag{8a}$$

$$y=q\chi_0^{\pm a},\quad a=\nu/\gamma=(2-\eta)^{-1}\ , \tag{8b}$$

which are similar to Eqs. (1a) and (1b) for $\chi^{\pm}(\tau,E)$: $g_{\pm}(y)$ and $h_{\pm}(y)$ are the corresponding scaling functions, ν is the critical exponent for inverse correlation length, η describes the power-law behavior of $\chi^{\pm}(\tau,q)$ on the critical isotherm, $\chi^{\pm}(0,q)\sim q^{\eta-2}$.

The Landau universality class is defined by the free energy $F=\frac{1}{2}C_2\tau P^2+\frac{1}{4}C_4P^4$, where C_2 and C_4 are some positive constants. In this case we have found[4] the susceptibility scaling function $f_{\pm}(y)$. Here we have reported only the results related to Eqs. (2b)–(2f). Below the critical point there is a trivial solution $y_1=0$ of Eq. (2a) for $f_-(y)$ and $\chi^-(\tau,E)$ does not have an extremum. Above the critical point there is a maximum and we have one nonzero-solution y_1 of Eq. (2a) for $f_+(y)$ as well as constant A_1 and universal quotient Q_1:

$$y_1=(4/(3^3C_4^{1/2}),\quad A_1=2^{1/3}/3C_4^{1/3},\quad Q_1=2\ , \tag{9a}$$

where $C_4/4$ is the coefficient of P^4 in the Landau free energy. We also have for this case Eq. (2c) in the form

$$\tau_1^{3/2}=(27C_4/16C_2^3)^{1/2}E\ . \tag{9b}$$

To the best of our knowledge there are no exact solutions for the simplest Ising model and $d\geq 2$ in a nonzero magnetic field. Several terms of the expansion for the Gibbs potential in powers of magnetic field above and below the critical point are given.[5] These expansions can be used to express the series for universal quotient $\chi^{\pm}(\tau,E)/\chi_0^{\pm}$ by four Watson invariants[6] (universal combinations of critical amplitudes of susceptibility). The situation is much easier in the case of the correlation function $\chi^{\pm}(\tau,\mathbf{q})$ for the Ising and Heisenberg models, where both approximate[7] and exact ($d=2$) (Ref. 8) calculations for $\chi^{\pm}(\tau,\mathbf{q})$ were carried out. The version ($q\sim\tau_m^{\nu}$) of the power law (2c) for the correlation function was first predicted theoretically in Ref. 7 for the Ising model. This prediction of maxima of $\chi^+(\tau,\mathbf{q})$ was next confirmed in neutron scattering experiments.[9] The maxima have also been observed experimentally in studies on nonzero-field susceptibility and specific heat for magnetic[10–12] and ferroelectric systems.[13] The susceptibility maxima usually appear in the higher-symmetry phase and they are the result of switching on a symmetry-breaking (electric, magnetic, etc.) field which is required to establish the symmetry of the ordered (less symmetric) phase.

EXPERIMENT

In Fig. 1 we present our experimental results obtained for ferroelectric triglycine sulfate (TGS). The measurement technique has been described in a separate paper.[14]

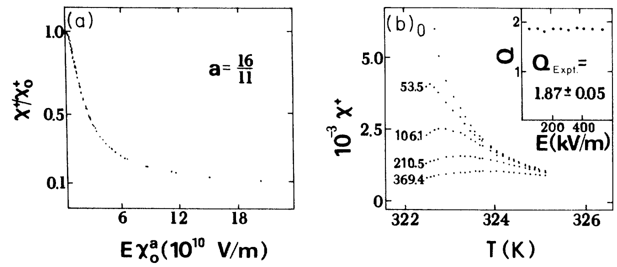

FIG. 1. The same experimental data for TGS presented in two systems of coordinates; (a) χ^+/χ_0^+ vs $E\chi_0^{+a}(a=1.46\simeq\frac{16}{11})$ for the 23 temperatures from the interval corresponding to $5\times10^{-4}<T/T_c-1<10^{-2}$ and for four values of the electric field E: 53.5, 106.1, 210.5, and 369.4 kV m^{-1} for each temperature; (b) χ^+ (E=const) vs T for the same, as in (a) values of T and E; the electric field values are given in kV m^{-1}. Inset: values of Q for various electric fields E for the other TGS sample; the average value of Q is 1.87±0.05. Both the measuring field (of frequency 1 kHz and amplitude not exceeding 10^3 V m^{-1}) and the constant external electric field E were applied parallel to the ferroelectric axis of the tested TGS crystals. For both samples the electrodes completely covered the crystal surfaces.

In Fig. 1(a) the experimental susceptibility scaling function χ^+/χ_0^+ versus $E\chi_0^{+a}$ [see Eqs. (1)] for the critical index $\delta=\frac{73}{23}\simeq 3.2$ (i.e., for $a=\delta/(\delta-1)=1.46\simeq\frac{16}{11}$ is shown. For the same experimental data, i.e., for the same temperature and electric-field values, the temperature dependences of susceptibility $\chi^+(T)$ were determined. The results are presented in Fig. 1(b). From the data presented in Figs. 1(a) and (1b) the following experimental facts for TGS may be concluded.

(i) Agreement between the experimental data and the static scaling hypothesis [Fig. 1(a)] and also the existence of susceptibility maxima [Fig. 1(b)]; for the given value of the electric field $E\neq 0$ only one susceptibility maximum was recorded.

(ii) Values of susceptibility lying on both sides of the maximum on Fig. 1(b) form one scaling function f_+; hence the existence of susceptibility maxima for various $E\neq 0$ cannot be associated with shifting of the critical temperature induced by the electric field [cf. general conclusions below Eq. (6)].

(iii) Within the limits of experimental error, the value of quotient Q is constant and independent of E [see inset in Fig. 1(b)]. The experimental value we obtained for Q ($=Q_{\text{expt}}$) as the mean value for various E, was $Q_{\text{expt}}=1.87\pm0.05$, and is thus slightly smaller than that predicted by mean-field theory (9a), i.e., $Q=2$. Both the value $\delta>3$ required to form the scaling function, as in Fig. 1(a), and the value Q_{expt} are examples of experimental results obtained for TGS which are inconsistent with mean-field theory (MFT). We have also found larger deviations from the MFT value $Q=2$ for other ferroelectric systems. These results will be presented in separate papers.

CONCLUSION

We suggest here the desirability of measuring these new invariants (2f) for different physical systems and various physical quantities (susceptibility, specific heat, and correlation function) at the maximum of the corresponding function. Maxima as well as minima of nonzero-magnetic-field susceptibility have been observed below the critical point for certain ferromagnets.[11] There are several factors such as demagnetization, electrode layers, etc., which make the measurement of exponent δ on the critical isotherm difficult and rather inaccurate. The form (1a) and (1b) of the susceptibility has been used to achieve precise measurement[14] of exponent δ from the data $[\chi_0^{\pm}(\tau), \chi^{\pm}(\tau,E),E]$ beyond the critical isotherm. The value of δ was selected from the condition of minimum scatter of the points on the plot $\chi^{\pm}(\tau,E)/\chi_0^{\pm}(\tau)$ versus $y=E\chi_0^{\pm}(\tau)^{\delta/(\delta-1)}$. We also suggest here using the same method for measurement of quotients Δ/α ($\alpha\neq 0$) and $\nu/\gamma=(2-\eta)^{-1}$ from Eqs. (7a) and (7b) and (8a) and (8b), respectively.

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