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A non-classical Widom form of the equation of state for triglycine sulphate (TGS) ferroelectric

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Abstract. A Widom form of the equation of state taking into account non-Landau invariants for triglycine sulphate (TGS) ferroelectric is proposed. The experimental values of the invariant Q and the exponents δ and γ are crucial for the determination of this equation. It is shown to be not derivable from the existing theories based on the renormalization group and ε-expansion and represents very well the experimental susceptibility data above and below T_C. The analytical properties of the proposed theory are compared with Landau and Domb–Hunter expansions. A method of determining the invariant Q from the experimental susceptibility scaling function is demonstrated on TGS and deuterated triglycine selenate ferroelectrics used as examples.

1. Introduction

Phase transitions near the critical point are described by a set of parameters called critical invariants [1–4]. We have in mind critical exponents, definite combinations of critical amplitudes for spontaneous polarization, susceptibility, specific heat and the amplitude describing the power-law dependence relating the external electric field, E, to the polarization, P, at the critical point ($T = T_C$) etc. Most of these invariants concern the behaviour of the polarization, the susceptibility and the specific heat in zero field. There are as well universal constants characterizing the behaviour of these quantities in non-zero electric field, like the exponents δ and Δ, and the Watson [5] and Q-invariants [6]. A direct theoretical calculation and/or experimental measurement of the zero-field invariants does not require the knowledge of the equation of state but it is indispensable in the theory for determining invariants such as δ, Δ and in particular Q. Even though the invariant Q does not occur explicitly, like δ does, in the known theoretical equations of state [1–3, 7–9], its value depends strongly on the functional form of the equation of state since it is calculated by equating to zero the third-order derivative, $\partial^3 G(\tau, E)/\partial E^2\,\partial\tau$, of the Gibbs potential G [6].

Analysing the experimental data on the susceptibility, χ, measured at a fixed electric field, E, for continuous phase transitions [6] or at a constant distance from the critical isopolare for discontinuous ones [10], it is very useful to investigate the ratio [6]

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

where $\tau_m = T_m/T_c - 1$ is the reduced temperature at which the susceptibility, $\chi(\tau, E)$, reaches a maximum at constant field, E, on changing τ above the critical temperature T_c ($T_m > T_c$). If Q is independent of E, it will become the non-zero-field critical invariant [6]. Any system with a constant value of Q has to satisfy the static scaling hypothesis [6]. Knowledge of the experimental value of Q is very important if one is to find the best approximate equation

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of state for the system investigated, as a very strong relation between (i) the value of Q and the non-linearities, generated by inserting particular susceptibility experimental scaling functions into the sequence of test equations of state (derived from the Domb and Hunter scaling hypothesis [3]), and (ii) particular experimental data has been ascertained [11, 12].

The most obvious, but trivial way to calculate Q is to do it using the definition [6]. There are, however, some disadvantages: (1) we need a lot of characteristics to achieve sufficient statistics for calculating a reliable value of Q; (2) the fits of the characteristics have to be perfect, which is not always easy to achieve; (3) measurements are often carried out at fixed temperatures, which makes this method useless.

The algorithm presented in this paper is free from the above drawbacks and is applied to TGS and DTGSe ferroelectrics. It is based on the experimental susceptibility scaling function, which can be created using constant-field or isothermal measurements for continuous phase transitions which happen to occur in TGS ferroelectric. If the transition is a discontinuous one, like in DTGSe ferroelectrics [13], an appropriate scaling function can be constructed from isothermal data only [10]. A determination of the invariant Q from the experimental scaling function is in fact an estimation of the mean value Q from all measurements made at constant field or constant temperatures simultaneously. Let us point out that the calculation of Q from one particular isotherm, in contrast to one constant-field characteristic, is impossible.

The authors of [14] have concluded that their isothermal experimental data on the polarization versus the electric field above and below T_C for TGS ferroelectric scale according to the Landau equation of state. On the other hand, there are experimental data [15–17] on the initial susceptibility for TGS ferroelectric which contradict the consequences of the Landau equation of state. From this theory it follows that the ratio (Γ^+/Γ^-) of the critical amplitudes of the susceptibility in zero electric field above (Γ^+) and below (Γ^-) T_C is equal to 2. Additionally, a different invariant, Q, also takes the value 2 [6], while the experimental observations deliver values larger and smaller than 2 for the quotient Γ^+/Γ^- [16,17] and Q [6], respectively. The following values: 2.3, 2.42, 2.7 and 3.0 of Γ^+/Γ^- for TGS ferroelectric were observed. The departures from the Landau theory [16,17] for this invariant were confirmed [18] as well. These initial susceptibility results hint that one can expect deviations from the Landau equation of state if it is transformed to the equivalent form putting together the initial susceptibility χ_0 $(=\chi(T,0))$, the non-zero-field susceptibility $\chi(T,E)$ and the external field E. Such equations, reported in [19,20], were used in [18] to provide clear evidence against the applicability of Landau theory to TGS ferroelectric: namely, that the isothermal experimental susceptibility data for the paraelectric and ferroelectric phases do not form one straight line (see figure 2 in [18]) when inserted into the corresponding Landau equation of state, equation (3*a*) or (3*b*) in [18]. The observed splitting of isotherms with their small non-linearities just goes to show that the exponent $\delta \neq 3$ and higher-order terms are expected in the equation of state. The results from [18] are consistent with the earlier ones [11, 12, 21] where non-linearity of the Landau equation of state, expressed in terms of the ratio χ_0/χ versus $E\chi_0^{\delta/(\delta-1)}$, was stated for the non-Landau value 3.17 of the exponent δ. Moreover, a non-Landau value 1.87 of the invariant Q was observed [6]. Let us sum up the main experimental results for TGS invariants arising from susceptibility investigations: $\gamma = 1, \delta = 3.17, Q = 1.87, \Gamma^+/\Gamma^- > 2$. Therefore all of these invariants with the exception of γ appear to be non-Landau ones. So, small deviations from the Landau theory of continuous phase transitions cannot be derived from any theory based on the renormalization group and ε-expansion [7,8] or from the analysis of series expansions by means of Padé approximants for Ising and Heisenberg models. The logarithmic corrections to the classical exponents in the Larkin–Khmelnitskii equation of state [22] were approximately replaced by small exponents ($\ll 1$) in [21], but this has not produced linearity of the above equation of state for the TGS experimental susceptibility data. The equation obtained

was similar to the Domb–Hunter one [3], which represents critical behaviour and contains no crossover phenomena but is restricted to the high-temperature phase without any possibility of passing to below T_C. It is a limiting case of the Widom equation of state due to the Griffiths analyticity condition [2]. The non-linearity appearing in the modified Landau equation of state [21] was explained in [11, 12] as coming from the relatively small contribution of the P^6-power with respect to lower-order terms in the framework of the Domb–Hunter expansion. We show in this paper that the competition of the P^4- and P^6-terms from [11,12] in the scaling can be replaced with one power $|P|^{\delta+1}$, with the exponent value $\delta + 1$ (=4.17) between 4 and 6. This new model of the free energy consisting of two ingredients, P^2 and $|P|^{\delta+1}$, is simpler than previous ones based on Domb–Hunter scaling [3] and Larkin–Khmelnitskii [22] theories and represents very well all deviations from Landau theory. Furthermore, the equation of state proposed in this paper manifests itself in the Griffiths structure [2] of the Widom [1] equation of state, i.e., it is able to represent simultaneously both high- and low-temperature phases.

First, in section 2 we present a new model for TGS ferroelectric leading to non-Landau values of the basic critical invariants and susceptibility scaling function. In section 3 we show how to calculate Q from the polynomial fit of the scaling function for TGS and DTGSe ferroelectrics. The present theory is compared to Landau and Domb–Hunter ones in the fourth section where we also show that a non-integer exponent δ leads to non-analytical susceptibility above T_c. Watson invariants are worked out there in the framework of the proposed model for both phases.

2. The scaling hypothesis for TGS ferroelectric

Let us consider the following model of the free energy:

$$F = \frac{1}{2}C_2\tau P^2 + \frac{1}{\delta+1}C_{\delta+1}|P|^{\delta+1} \tag{1}$$

where the absolute value causes F to be an even function of P and the exponent δ is permitted to take on real values, $\delta \geqslant 1.5$. This model is postulated to give the exponent $\gamma = 1$ (cf. equation (4)) which agrees with the experimental value for TGS ferroelectric [16–18]. Assuming additionally the experimental value 3.17 [6] for the exponent δ, it is shown (cf. equation (11)) that the invariant Q takes the value 1.85, which is very close to the experimental one, 1.87 [6], while the invariant Γ^+/Γ^- is equal to 2.2 (cf. equation (13)), which is not far from the lowest experimental value, 2.3 [16]. Expression (1) leads to the equation of state

$$E = \partial F/\partial P = P(C_2\tau + C_{\delta+1}|P|^{\delta-1}) \tag{2}$$

and the inverse susceptibility ($\chi = \partial P/\partial E$)

$$1/\chi = C_2\tau + \delta C_{\delta+1}|P|^{\delta-1} \tag{3}$$

where C_2 and $C_{\delta+1}$ are assumed to be positive constants, $\tau = T/T_c - 1$ and the exponent δ characterizes the power-law relation between the electric field E and the polarization P on the critical isotherm $\tau = 0$.

Equation of state (2) can be rewritten in the scaling form of Widom and Griffiths [1, 2]: $E = P|P|^{\delta-1}g(z)$, with $g(z) = C_{\delta+1} + C_2 z$, where $z = \tau/|P|^{1/\beta}$, $\gamma = 1, \delta = 3.17$, $\beta = \gamma/(\delta - 1) = 0.46$ (see also section 4). Close inspection of the literature [7, 8] clearly indicates that the Widom and Griffiths forms of the equation of state and invariants in the zero-order approximation ($\varepsilon = 0, d = 4$) of the renormalization group method have the Landau form. However, there is a significant difference between the corresponding results in the first-order approximation ($\varepsilon = 1, d = 3$) and those for TGS ferroelectric reported above.

Thus the proposed equation of state (2) is excluded and cannot be derived from the existing theories [7, 8]. This indicates a non-perturbative nature for equation (2) for TGS ferroelectric.

Equations (1)–(3) contain the known mean-field cases of continuous phase transitions: Landau critical ($\delta = 3, \gamma = 1, \beta = 0.5$), tricritical ($\delta = 5, \gamma = 1, \beta = 0.25$) and higher-order critical points [11], as well as the percolation problem [23] ($\delta = 2, \gamma = 1, \beta = 1$), which is equivalent to the s-state Ashkin–Teller–Potts (ATP) model [24]. The exponent δ is an integer in the above mean-field theories. In this paper we consider two ferroelectric systems (TGS and DTGSe with nearly 100% deuterium content) with non-integer δ and show equations (1)–(3) to be nearly exact for TGS ferroelectric. Equation (1) will be non-analytical in the order parameter, P, if δ is not an integer, because practically all derivatives of F with respect to P are divergent when the critical point ($P = 0, \tau = 0, E = 0$) is approached.

There is one solution (paraelectric), $P = 0$, of equation (2) above T_c ($\tau > 0$) at $E = 0$. Therefore the zero-field susceptibility, χ_0^+, takes the form of the Curie–Weiss law:

$$1/\chi_0^+ = C_2\tau^\gamma \qquad \gamma = 1 \qquad T > T_c \tag{4}$$

which has been evidenced experimentally for TGS ferroelectric [16–18]. Having eliminated the polarization from equation (3) and temperature, τ, using equation (4), one can transform equation of state (2) to the scaling form

$$K(\delta, \chi_0^+/\chi) = (\chi_0^+/\chi - 1)(\chi_0^+/\chi + \delta - 1)^{(\delta-1)} = \delta^\delta C_{\delta+1} E^{(\delta-1)} (\chi_0^+)^\delta \tag{5}$$

which describes a system in the paraelectric phase ($T > T_c$). Such an equation of state where τ is expressed in terms of χ_0^+ and the polarization by $\chi(\tau, E)$ has not previously been reported, to the best of our knowledge, within the renormalization group approach for any case. It follows from this formula that the ratio χ/χ_0^+ is a function of $E(\chi_0^+)^{\delta/(\delta-1)}$:

$$\chi/\chi_0^+ = f(x) \qquad x = E(\chi_0^+)^a \qquad a = \delta/(\delta - 1) = \Delta/\gamma \tag{6}$$

where the gap exponent Δ determines [6] the power-law relation, $E \propto \tau_m^\Delta$, between the electric field E and temperature (τ_m) of the maximum of χ. It is impossible to find an explicit form of $f(x)$ for an arbitrary value of δ in the case of relation (5). Equation (6) results also from the scaling hypothesis [1–3, 6], which is independent of any particular model.

We now derive an equation for $Q = \chi_0^+(\tau_m)/\chi(\tau_m, E)$, differentiating the first and the second relations in equation (6) with respect to τ assuming a constant field E and $\partial\chi/\partial\tau = 0$. It is given by

$$G(x) = f(x) + ax\,\mathrm{d}f(x)/\mathrm{d}x = 0. \tag{7a}$$

Having estimated the root, x_0, of the algebraic equation $G(x) = 0$, one can calculate Q from the scaling function f:

$$Q = 1/f(x_0). \tag{7b}$$

Another form

$$x = (\delta^\delta C_{\delta+1})^{-1/(\delta-1)}(1/f - 1)^{1/(\delta-1)}(1/f + \delta - 1) \tag{8}$$

of equation (5) is very useful for finding the function $G(x)$. Taking into account relations (6) and differentiating the last equation with respect to x, we get the result

$$\mathrm{d}f(x)/\mathrm{d}x = -[(\delta^\delta C_{\delta+1})^{1/(\delta-1)}/a]f^3(1/f - 1)^{(1-1/(\delta-1))} \tag{9}$$

for the derivative of the function f.

Equations (8) and (9) can be used to derive the function G defined in equation (7a) in the parametric form

$$G(x) = f^2[f(\delta - 1) - (\delta - 2)] \tag{10}$$

where x is to be calculated using equation (8) and f to be varied in the interval [0, 1]. If $G(x_0) = 0$, the expression in the square brackets in equation (10) will vanish. Then the invariant Q may be expressed in terms of the exponent δ:

$$Q = (\delta - 1)/(\delta - 2) \tag{11}$$

derived from equation (7*b*). This simple relation between Q and δ holds only for the two terms of the free energy in (1) and will become more complicated when additional components appear on the right-hand side of equation (1). Formula (11) provides Q for the following theoretical cases: Landau critical ($Q = 2$), tricritical ($Q = 4/3$) and higher-order critical points [11]. Using the mean-field free energy close to T_c for the ATP model from [24], and equation (11), we predict Q to be undefined ($Q = \pm\infty$) in this case and in the percolation problem ($\delta = 2$). Of course, fluctuations should make this value finite. Their influence is that of adding higher-order terms on the right-hand side of equation (1).

The experimental value of δ for TGS ferroelectric was found to be the same in constant-temperature [25] and constant-field [6] measurements, $\delta = a/(a-1) \simeq 3.17$ ($a = 1.46$). Inserting it into equation (11) and using equation (7*b*), we obtain $f(x_0) = 0.54$ and the theoretical value $Q_{th} = 1.85$, which is very close to the experimental one [6], $Q = 1.87$, for the system considered. The small difference, $\Delta Q = Q - Q_{th} = 0.02$, indicates that the free-energy model (1) represents the TGS ferroelectric almost exactly. This prediction is confirmed in figure 1(a) showing the function K from equation (5) versus $E^{\delta-1}(\chi_0^+)^\delta$ as the straight (solid) line. Here, the experimental data for χ_0^+, χ, E and δ ($\simeq$3.17) in the form (6) of the scaling function from [25] have been used and are represented in figure 1(a) as open circles. The coefficient of proportionality, $\delta^\delta C_{\delta+1}$, in equation (5) is estimated as

$$\delta^\delta C_{\delta+1} = 5.0241 \times 10^{-22}\ \mathrm{m}^{\delta-1}\ \mathrm{V}^{-(\delta-1)} \tag{12}$$

using linear regression. Inserting this value and $f(x_0) = 0.54$ into equation (8), we find the root $x_0 = 2.346 \times 10^{10}\ \mathrm{V\ m^{-1}}$ of equation (7*a*). The point $[x_0, f(x_0)]$ of the scaling function $f(x)$ represented by the cross in figure 1(b) generates maxima of all constant-field characteristics.

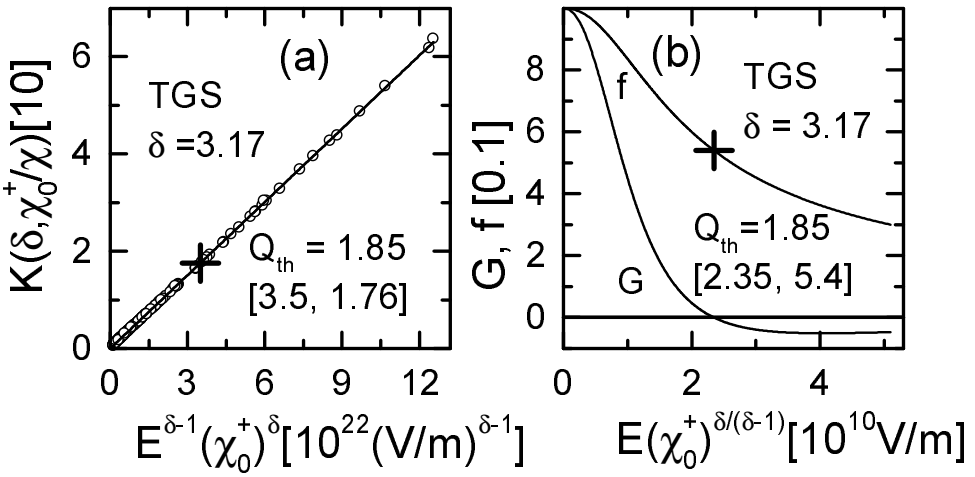

Figure 1. (a) The function $K(\delta, \chi_0^+/\chi)$ from equation (5) versus $E^{\delta-1}(\chi_0^+)^\delta$ for TGS experimental data (χ_0^+, χ, E, $a = 1.46$, $\delta = (a/(a-1))$ taken from [25]: open circles—experimental data; solid line—fitting of K to a straight line with the coefficient, $\delta^\delta C_{\delta+1}$, given in equation (12). (b) The functions $f(x)$ and $G(x)$ calculated from equations (6), (8), (10) and (12).

Here, the functions $f(x)$ and $G(x)$ from equation (10) are plotted as solid lines, where x has been calculated according to equations (12) and (8), varying f in the interval [0, 1]. The point in figure 1(a) marked by the cross is linked to the corresponding one in figure 1(b) as follows: $[x_0^{\delta-1}, K(\delta, 1/f(x_0))]$. These points show the corresponding location of the universal constant Q.

Now we show that the invariant Γ^+/Γ^- calculated from the model (1) and for the experimental value $\delta = 3.17$ is greater than 2. Assuming $E = 0$ in equation (2) we find the spontaneous polarization

$$|P| = [(C_2/C_{\delta+1})(-\tau)]^{\beta} \qquad \beta = 1/(\delta - 1) = 0.46.$$

Inserting this expression into equation (3) we get the zero-field susceptibility (χ_0^-):

$$1/\chi_0^- = C_2(\delta - 1)(-\tau)$$

below T_C. Taking into account this formula and equation (4) we obtain the universal constant

$$\Gamma^+/\Gamma^- = \delta - 1 \simeq 2.2. \tag{13}$$

Using the above formula for χ_0^- and (3), one can rewrite equation of state (2) in the following scaling form below T_c:

$$(\chi_0^-/\chi - 1)[\chi_0^-/\chi + 1/(\delta - 1)]^{1/(\delta-1)} = (\delta^{\delta} C_{\delta+1})^{1/(\delta-1)} E(\chi_0^-)^{\delta/(\delta-1)}. \tag{13a}$$

The experimental invariants δ and Q for the DTGSe ferroelectrics have been obtained previously [10] and are given by

$$\delta = 1.5 \qquad Q \simeq 1.2 \qquad \text{DTGSe}. \tag{14}$$

We now demonstrate that the model (1) cannot describe this system correctly. The arguments are the following. Let us calculate the theoretical value of Q in this case from (11) taking the foregoing experimental value of δ. We obtain the result $Q_{th} = -1$ for the DTGSe system. It does not agree with its experimental counterpart Q reported in equation (14). Therefore one cannot expect linearity of the function K from equation (5) versus $E^{(\delta-1)}(\chi_0^+)^{\delta}$ when inserting into K the corresponding experimental scaling functions in the form (6) from [10]. The non-linearity of K for the DTGSe system should be very strong because a substantial difference between the experimental, Q, and theoretical, Q_{th}, values is detected in this case: $\Delta Q = 2.2$. It can be predicted by modifying the method described in section 4, from [11], for the present function K from equation (5) (i.e., assuming that $K = d_1 x + d_2 x^2$) that the function K is convex for $Q > Q_{th}$. And this is confirmed in figure 2. In consequence, an equation of state for the DTGSe system will be more complicated than one for the TGS system. Additional higher-order terms must be included on the right-hand side of equation (1) to achieve linearity of K. It should be mentioned that scaling with exponents of similar character ($2 \geqslant \beta \geqslant \gamma \geqslant 1$) to those for the DTGSe system has been discovered in the quantum $Sr_{1-x}Ca_xTiO_3$ (SCT) ferroelectrics [27] recently. There is also a theoretical paper [9] where the possibility of the exponent β being greater than 1 is encountered in connection with an investigation of the equation of state for Ising-type random-bond spin glass in $6 - \varepsilon$ dimensions with the aid of renormalization group recursion relations.

In this section, arguments have been given regarding how important knowledge of the experimental value of Q is. In the next section we demonstrate a way of determining Q from the experimental scaled data.

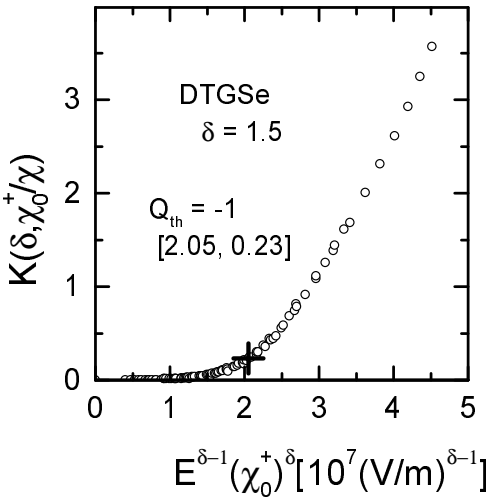

Figure 2. The function $K(\delta, \chi_0^+/\chi)$ from equation (5) versus $E^{\delta-1}(\chi_0^+)^\delta$ for DTGSe experimental data (χ_0^+, χ, E, $a = 3$, $\delta = (a/(a-1))$ taken from [10]: open circles—experimental data.

3. Q and the experimental scaling function

Now we will show how to calculate Q from the experimental scaling function f if the exact equation of state is unknown. Let us suppose that the function $f(x)$ can be fitted very smoothly by an Nth-order polynomial

$$f(x) = \sum_{n=0}^{N} A_n x^n \tag{15}$$

where the coefficients, A_n, remain to be determined from polynomial regression. Using equations (15) and (7a), we obtain the following polynomial representation of the function $G(x)$:

$$G(x) = A_0 + \sum_{n=1}^{N} (1 + an) A_n x^n \tag{16}$$

where a is the experimental invariant linked to δ in the third of relations (6).

In figure 3 we show the experimental scaling function f (open circles) for TGS [25] and DTGSe [10] ferroelectrics. Let us point out that the experimental data in figure 3(b) represent the right-hand branch ($E = h > 0$) of the unsymmetrical scaling function from figure 5 in [10] because maxima (and the invariant Q) are generated only at positive, constant distances, h, from the critical isopolare; cf. figure 4 in [10]. The continuous lines correspond to eighth-order polynomial fits carried out using the least-squares method. The fitting coefficients, A_n, from equation (15) are next inserted into equation (16) to give the function $G(x)$. It is plotted in figure 3 as a solid line. The solutions, x_0, of equation (7a) and corresponding values $f(x_0)$ are displayed in figure 3 in square brackets, $[x_0, f(x_0)]$. Q_{th} is then calculated from formula (7b): $Q_{th} = 1.85$ and 1.18 for TGS and DTGSe ferroelectric, respectively. The results obtained agree very well with experimental ones in all cases considered, as there are very small differences $\Delta Q = Q - Q_{th} = 0.02$ and 0.02 for TGS and DTGSe crystals, respectively. We have checked that x_0 is relatively stable with increasing order of polynomial, so we may treat its value as reliable.

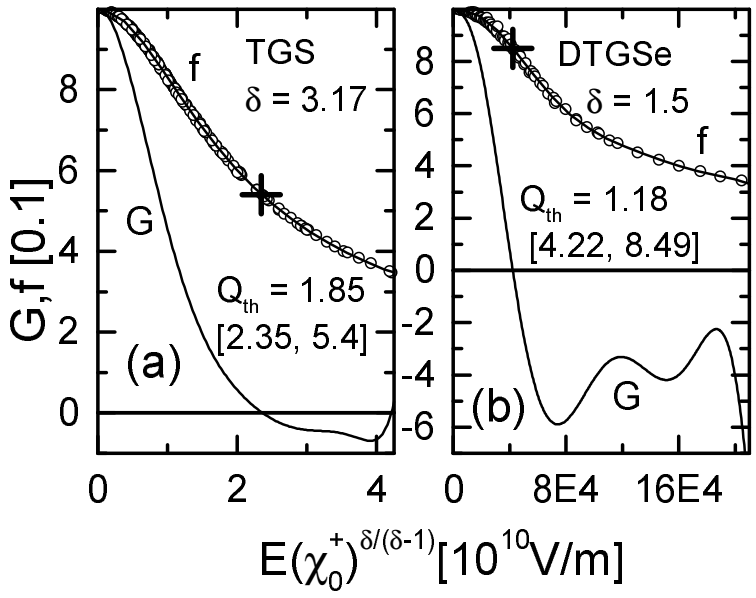

Figure 3. The scaling function $f(x)$ from equation (6): open circles—experimental data; solid line—eighth-order polynomial fit (15); and the function $G(x)$ calculated according to equation (16) with the fitting coefficient, A_n, from equation (15) and experimental data $(\chi_0^+, \chi, E, a, \delta)$, for: (a) TGS from [25]; (b) DTGSe from [10].

Examining the diagrams in figure 3 one can fault the functions G for their irregular behaviour for large arguments and the existence of additional finite solutions of equation (7*a*). In figure 3(a) we show two roots. They would appear also in figure 3(b) if a further order in the fitting polynomials were considered. These results contradict the one value of Q observed in the experiments [6, 10, 26]. Therefore the polynomial fittings of $f(x)$ in figure 3 are not good enough to give a sufficiently correct approximation of its derivative in equation (7*a*). The true picture of $G(x)$ for DTGSe crystal should be similar to that displayed in figure 1(b) for the TGS sample where $G(x)$ exhibits one finite root and then gains a negative minimum going afterwards to zero as x tends to infinity. To obtain such a behaviour for DTGSe crystal, the appropriate exact equation of state is required.

4. Consequences of non-integer δ

There is a difference between mean-field theory and the Landau theory of phase transitions. The traditional free energy of the mean field can be expanded into an infinite series (also called the Landau expansion)

$$F_m = \frac{1}{2}C_2\tau P^2 + \sum_{n=2}^{\infty}\frac{1}{2n}C_{2n}P^{2n} \tag{17}$$

where C_{2n} are constant coefficients while the Landau theory of continuous phase transitions is represented only by the first two terms of this series ($C_2 > 0$, $C_4 > 0$):

$$F_L = \frac{1}{2}C_2\tau P^2 + \frac{1}{4}C_4P^4. \tag{18}$$

This expression describes the Landau universality class with the following basic critical invariants: $\gamma = 1$, $\beta = 1/2$, $\delta = 3$, $\Delta = 3/2$, $\Gamma^+/\Gamma^- = 2$ and $Q = 2$. If just the coefficients C_2 and C_6 are assumed to be different from zero, this will lead to the Landau theory of the tricritical point with the fundamental critical invariants: $\gamma = 1$, $\beta = 1/4$, $\delta = 5$, $\Gamma^+/\Gamma^- = 4$ and $Q = 4/3$. It is also possible to consider further cases with two coefficients different from zero: $C_2 \neq 0$ and $C_{2n} \neq 0$ for $n = 4, 5, \ldots$. The enumerated two-component combinations guarantee the scaling whereas ones with three and more components which must include the P^2-term do not satisfy the scaling demands because of their multicriticality (crossover phenomena) [11].

Therefore, subsequences with three and more ingredients from the series (17) (for instance combinations of P^2-, P^4- and P^6-terms) are not suitable for the description of a physical system (like our TGS one) whose experimental data have been presented in the form of a scaling function; this is an indication that the system may have just one critical point. To depict such an object using a series like (17), the multicriticality must be removed. This has been done by Domb and Hunter [3]. Investigating high-temperature series expansion for the Ising model by means of Padé approximants, they predicted the following form of the free energy:

$$F_{DH} = \frac{1}{2} C_2 \tau^{\gamma} P^2 + \sum_{n=2}^{\infty} \frac{1}{2n} C_{2n} \tau^{(2n-1)\gamma - 2(n-1)\Delta} P^{2n} \tag{19}$$

which characterizes behaviour with only one critical point. It should be pointed out that the exchange of C_{2n} in (17) for $C_{2n}\tau^{(2n-1)\gamma-2(n-1)\Delta}$ in (19) eliminates the multicriticality involved in this equation. The multiplication of the temperature coefficients by P^{2n} arises from short-range-order interactions. The exponents of τ in the P^4-, P^6- and P^8-terms have the following values: 0.08, -0.84, -1.76 for the experimental values $\gamma = 1$, $\delta = 3.17$, $\Delta = 1.46$ used in this paper: the higher the index $(2n)$ of P, the more negative the exponent of τ. If we cut the series (19) off at the P^6-term, the susceptibility χ would vanish at T_c in non-zero electric field, but this contradicts the experimental power law, $\chi \sim E^{-(\delta-1)/\delta}$, at T_c. Such an unphysical result would be avoided if the sum of the infinite number of divergent terms in equation (19) were able to give the power law $E \sim P|P|^{\delta-1}$, i.e., finite values at T_c. Moreover, the series (19) possesses a branch point which makes going below T_c impossible. Fortunately, Widom's proposal [1] in the Griffiths-disguised form [2] $E = P|P|^{\delta-1} g(z)$ (where $z = \tau/|P|^{1/\beta}$) of the equation of state shows how to go from above to below T_c, making simultaneous description of high- and low-temperature phases possible. Here the function $g(z)$ should be a real, positive and analytic one for z in the interval (z_0, ∞), where $z_0 < 0$ and the condition $g(z_0) = 0$ defines the boundary separating the one- and two-phase regions. This border is a curve on the (P, τ) plane represented by the formula $z_0 = \tau/|P|^{1/\beta}$ for zero-field (spontaneous) polarization. The function $g(z)$ can be transformed to the form

$$|P|^{-\delta} \sum_{n=1}^{\infty} C_{2n} \tau^{(2n-1)\gamma - 2(n-1)\Delta} |P|^{2n-1}$$

for $\tau > 0$ and $P > 0$ according to equation (15) in the paper [2] by Griffiths. Multiplying the above series by $P|P|^{\delta-1}$ one obtains the same equation of state as arises from the Domb and Hunter free energy (19).

The present equation of state (2) can be rewritten in the Griffiths form [2]

$$E = P\,|P|^{\delta-1}\, g(z) \qquad g(z) = C_{\delta+1} + C_2 z \qquad z = \tau/\,|P|^{1/\beta} \tag{20}$$

where $\gamma = 1$, $\delta = 3.17$, $\beta = \gamma/(\delta - 1) = 0.46$. Thus $g(z)$ is a real, positive and analytic function for z in the interval $z_0 < z < \infty$, where $z_0 = -C_{\delta+1}/C_2$—that is, it meets the demands

given on page 180 in [2]. The series (19) can have physical meaning if all of its terms that are divergent at $\tau = 0$ are the effects of a special function expansion with its finite value at T_c. In this case the function (19) does not diverge at the critical point ($P = 0, \tau = 0, E = 0$) like the functions (1) and (20). However, all the derivatives of fifth and higher orders with respect to P of the free energies (19) and (1) are divergent at the critical point ($P = 0, \tau = 0, E = 0$). Therefore we have sufficient grounds for stating that the free energy (1) with two terms does not represent the infinite series (17) for the mean field. One could have the impression that the series (19) is a good effective interpolation for (1) above T_c for $P > 0$. We show below that such thinking is erroneous. The susceptibility series calculated from (19) should be a function of E^2 while that derived from (1) is found below to depend on $E^{\delta-1}$.

The component $|P|^{\delta+1}$ in equation (1) causes divergencies of susceptibility derivatives of third and higher order to arise at the limit $E = 0$. This is clear from equation (5), where the electric field E appears with the even, non-integer exponent $\delta - 1 = 50/23 \simeq 2.17$, $E^{\delta-1}$. This is why the susceptibility χ has to be expanded not in powers of E^2 but in powers of $H = E^{\delta-1}$ as follows:

$$\chi = \chi_0^+ + \chi_1^+ H^1 + \chi_2^+ H^2 + \chi_3^+ H^3 + \cdots \qquad H = E^{\delta-1} \qquad T > T_c. \quad (21)$$

This series can be expressed in terms of invariants $W_n^+ = \chi_{n+1}^+ (\chi_0^+)^n / (\chi_1^+)^{n+1}$ $(n = 1, 2, \ldots)$, proportional to Watson ones [5], above T_c:

$$\chi / \chi_0^+ = 1 + y + \sum_{n=1}^{\infty} W_n^+ y^{n+1} \qquad y = H \chi_1^+ / \chi_0^+. \quad (22)$$

Inserting this sum into formula (5) and expanding the expression $(\chi_0^+ / \chi + \delta + 1)^{\delta-1}$ in powers of y, one can obtain the formulae

$$\chi_1^+ / \chi_0^+ = -(\delta C_{\delta+1} / C_2^{\delta}) / \tau^{\Delta(\delta-1)} \quad (23)$$

and

$$\begin{aligned} W_1^+ &= (2\delta - 1)/\delta \\ W_2^+ &= (9\delta^2 - 9\delta + 2)/(2\delta^2) \\ W_3^+ &= (32\delta^3 - 48\delta^2 + 22\delta - 3)/(3\delta^3) \end{aligned} \quad (24)$$

for a few initial invariants W_n^+ by comparing the coefficients on the two sides of (5) for the same powers of y. The values of these quantities for the Landau model (18) and the TGS one ($\delta = 3.17$) are the following: $W_1^+ = 5/3 \simeq 1.67$, $W_2^+ = 28/9 \simeq 3.11$, $W_3^+ = 59/9 \simeq 6.11$ and $W_1^+ \simeq 1.68$, $W_2^+ \simeq 3.18$, $W_3^+ \simeq 6.32$, respectively. There are also two sets of Watson invariants below and at T_c, but we restrict ourselves to the low-temperature case. From equation (13*a*) it is clear that susceptibility for $T < T_c$ is a function of E, i.e., it can be expanded in powers of E as follows:

$$\chi = \chi_0^- + \chi_1^- E^1 + \chi_2^- E^2 + \chi_3^- E^3 + \cdots \qquad T < T_c. \quad (25)$$

One can introduce the low-temperature invariants, $W_n^- = \chi_{n+1}^- (\chi_0^-)^n / (\chi_1^-)^{n+1}$ $(n = 1, 2, \ldots)$, proportional to Watson ones, into the series (25):

$$\chi / \chi_0^- = 1 + y + \sum_{n=1}^{\infty} W_n^- y^{n+1} \qquad y = E \chi_1^- / \chi_0^-. \quad (26)$$

Inserting this sum into the left-hand side of equation (13*a*) and expanding it in powers of y we find the relation

$$\chi_1^- / \chi_0^- = -[\delta/(\delta - 1)](C_{\delta+1} / C_2^{\delta})^{1/(\delta-1)} / (-\tau)^{\Delta} \quad (27)$$

and a few invariants W_n^-:

$$\begin{aligned} W_1^- &= (\delta + 1)/\delta \\ W_2^- &= (2\delta^2 + 5\delta + 2)/(2\delta^2) \\ W_3^- &= (3\delta^3 + 13\delta^2 + 13\delta + 3)/(3\delta^3). \end{aligned} \tag{28}$$

Their values for the Landau model ($\delta = 3$) and the TGS one ($\delta = 3.17$) are given by $W_1^- = 4/3 \simeq 1.33$, $W_2^- = 35/18 \simeq 1.94$, $W_3^- = 80/27 \simeq 2.96$ and $W_1^- \simeq 1.32$, $W_2^- \simeq 1.89$, $W_3^- \simeq 2.83$, respectively. The above comparison of the invariants $W_n^\pm$ given below formulae (24) and (28) shows that the present model high- and low-temperature invariants ($\delta = 3.17$) are higher and lower than their Landau counterparts, respectively.

5. Conclusions

The proposed non-Landau model (1) for ferroelectric TGS is very simple, non-analytical in the order parameter and non-perturbative. It cannot be derived from the existing theories based on renormalization group calculations. To our knowledge, nobody has found an exact solution even for the simplest cases—for example, the two-dimensional short-range Ising-type model at non-zero external field. It is not clear at the present time what is so special about TGS from a microscopic point of view that it would explain the form (1) of the free energy. Even if one knew exactly which microscopic mechanism led to the non-analytical behaviour of TGS, it would still be more difficult to find an exact solution than for the simplest Ising case. The equation of state resulting from (1) possesses the Widom–Griffiths structure, and the two constant coefficients C_2 and $C_{\delta+1}$ are the same for both ferroelectric and paraelectric phases. It can be presented neither as a Landau expansion in mean-field theory nor as a Domb–Hunter one due to the Griffiths analyticity condition [2] because of the difference in the electric field behaviour of the susceptibility above T_c between these theories and the present one. In other words, the susceptibility arising from (17) and (19) is a function of E^2, but that derived from equation (1) depends on $E^{\delta-1}$, even having a non-integer exponent, $\delta - 1 = 50/23 \simeq 2.17$. Therefore, the susceptibility derivatives of all orders starting from the third one are divergent above T_c in the zero-field limit. But this does not mean that the susceptibility itself is divergent in this limit except when T is approaching to T_c. The low-temperature susceptibility is shown to be an analytic function of E. It is worth pointing out the similarities of and differences between the behaviours of our model and previous ones. The common feature of these theories is that the susceptibility is an analytic function of E below T_c in all cases. The difference in the behaviour of χ becomes apparent above T_c; χ is an analytic function of E^2 in the Landau and Domb–Hunter cases, whereas this is not so for our model. Using the experimental values of the exponents $\gamma = 1$ and $\delta = 3.17$, we predict from model (1) non-Landau values of the invariants $\Gamma^+/\Gamma^- > 2$ and $Q < 2$ observed in experiments. We have found also several Watson invariants characterizing the expansion of the susceptibility in powers of E and $H = E^{\delta-1}$ below and above T_c, respectively. The method used to determine the invariant Q from the experimental susceptibility scaling data is presented for two examples: TGS and DTGS ferroelectrics. It is stated that the nearly exact equation of state, in contrast to the approximate one, leads to a single value of the invariant Q, which should be very close to the experimental one.

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