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Singularities and scaling invariants of susceptibility in biasing field near critical point: application to uniaxial ferroelectrics

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Abstract
The general shape of the temperature dependence of the static susceptibility in a biasing field conjugated to the order parameter is analysed with the use of the simplest equation of state compatible with the Widom and Griffiths scaling hypothesis. The corresponding curves are demonstrated to show from two to four inflection points, from which a discontinuous inflection point is found to occur exactly at the critical point whenever the critical exponent of susceptibility differs from one: $\gamma \neq 1$. The unique inflection point occurring below the temperature of the maximum of the susceptibility in the case of the classical critical exponents, i.e. in the mean field theory, is also shown to be strictly independent of the biasing field. New scaling invariants related to the inflection points are found and their analytical expressions are given for the considered equation of state. The usefulness of the theoretical results to the analysis of experimental data is discussed.

1. Introduction

Measurements of susceptibility in conjugated biasing field provide information about the system in a two-parameter space: temperature T and field E. The critical point then can be approached from different directions in this space. This allows one to obtain a collection of critical parameters corresponding to a vicinity of the critical point without a need to approach the critical point itself too closely. The latter task is known to be rather difficult. Practical determination of the critical parameters requires an explicit equation of state relating the order parameter with the actual temperature and field. The scaling hypothesis [1–3] provides a framework for construction of the equations of state capable of describing non-classical critical

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behaviour. The corresponding critical exponents then fulfil some relations, called scaling relations, but need not belong to universality classes as required by the renormalization group theory [1]. In fact, the experimentally determined critical exponents for many known materials, for example, ferroelectrics, are significantly different from those predicted by the particular universality classes [4–6]. The specific form of the scaling equations of state implies a number of invariants [7] that can be extracted from the curves of the susceptibility measured as a function of temperature at different biasing fields. The invariants are in fact combinations of critical parameters such as critical exponents, critical temperature and critical amplitudes. In turn, the invariants depend neither on the external field E nor on the specific free energy coefficients. Therefore, they are a useful tool permitting one to extract the critical parameters from experimental data.

In the present work we study the general shape of the susceptibility curves in a biasing field conjugated to the order parameter for different values of the critical exponents within the simplest possible equation of state compatible with the scaling hypothesis. For the sake of specificity, in what follows, we will consider the electric polarization P as the order parameter and the electric field E as the conjugated field. Thus, our considerations apply directly to uniaxial ferroelectrics and to the measurements of the electric susceptibility in a biasing field, the phenomenon sometimes called the *nonlinear dielectric effect* (NDE). A discontinuity in the second derivative $\partial^2\chi/\partial T^2$, which is equivalent to a sharp inflection point, is found to be a signature of a non-classical value of the critical exponent $\gamma \neq 1$ in this kind of equation of state. The location of this sharp inflection point with respect to the critical temperature on the temperature axis and the arrangement of other inflection points of the susceptibility curves turn out to be a function of the critical exponents γ and δ. The regions in the plane (γ, δ) where the particular different arrangements are expected are presented in a diagram in section 2. In section 3 we discuss practical procedures to obtain useful invariants from the susceptibility curves. Apart from the invariants related with the maxima of the susceptibility curves, which are already known in literature [8, 9], we analyse invariants involving the inflection points. The corresponding explicit expressions for the scaling invariants are given.

2. Temperature dependence of the electric susceptibility measured at a biasing field near a paraelectric–ferroelectric phase transition

The simplest Gibbs free energy compatible with the Widom scaling hypothesis [1–3] for a uniaxial ferroelectric material reads

$$F = \frac{1}{2}a\,\mathrm{sgn}(\tau)|\tau|^{\gamma}P^2 + \frac{1}{\delta+1}b|P|^{\delta+1} - EP, \tag{1}$$

where $\tau = (T - T_C)$ is the reduced temperature, a and b are constant coefficients, P is the electric polarization (the order parameter) and E is the external electric field (variable conjugated to the order parameter). The quantities δ and γ are the critical exponents [1]. The condition for a minimum of the free energy of equation (1) with respect to P, $\partial F/\partial P = 0$, provides the scaling equation of state:

$$E = P\left(a\,\mathrm{sgn}(\tau)|\tau|^{\gamma} + b|P|^{\delta-1}\right). \tag{2}$$

The function on the right-hand side of equation (2) is a homogeneous function, as it should be in the scaling theory [1–3, 10]. With its two terms equation (2) is the simplest possible equation of state showing the homogeneity. The equation of state proposed in [10], also containing two terms, cannot be directly used without additional terms because it produces a divergent or zero susceptibility at zero field below the critical point when $\gamma < 1$ or $\gamma > 1$, respectively. For the classical values of the critical exponents $\gamma = 1$ and $\delta = 3$,

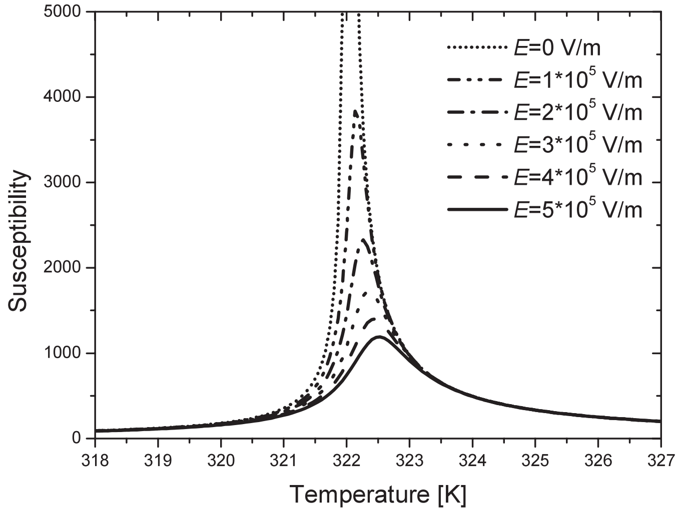

Figure 1. Temperature dependence of electric susceptibility in various biasing fields E according to equation (3) with critical exponents $\delta = 3.75$ and $\gamma = 0.98$, and parameters $a = 11.56 \times 10^7\ \mathrm{V^2\ mJ^{-1}\ K^{-0.98}}$, $b = 7.2 \times 10^{12}\ \mathrm{V^{4.75}\ J^{-3.75}\ m^{-6.5}}$ (similar to those from [11]) and $T_C = 322$ K.

equations (1) and (2) reduce to those known from the mean field or Landau theory [1]. For general, non-integer values of δ, equation (2) cannot be solved analytically. The most straightforward expression for the isothermal static susceptibility (in the units of the vacuum dielectric permittivity ε_0) is

$$\chi(\tau, P(\tau, E)) = \left(\frac{\partial P}{\partial E}\right)\bigg|_{\tau} = (a\,\mathrm{sgn}(\tau)|\tau|^{\gamma} + \delta b|P(\tau, E)|^{\delta-1})^{-1}, \qquad (3)$$

where $P(\tau, E)$ satisfies equation (2).

Figure 1 shows a theoretical example, obtained with equation (3), of the electric susceptibility χ as a function of temperature at several values of the biasing field. The parameters of the curves have been chosen in a realistic way to be comparable with the actual values observed in real experiments [11]. As one can note, the maximum of the susceptibility $\chi(\tau, E)$ shifts towards higher temperatures with increasing biasing electric field E. The condition for this maximum following from equation (3) is

$$\tau_{\max} = (b^{1/\delta} a^{-1} E^{(\delta-1)/\delta} \delta(\delta-2)(\delta-1)^{2(1-\delta)/\delta})^{1/\gamma}. \qquad (4)$$

Apart from the maxima, other characteristic points of the curves of figure 1 are inflection points. The latter correspond to maxima or minima of the first derivative of the susceptibility.

Figure 2 shows plots of the derivative $\partial\chi/\partial\tau$ versus temperature for some values of the critical exponents δ and γ. To make the features of the curves of figure 2 practically discernable an appropriate biasing field should be applied. If the field is too weak the maximum and all the inflection points lie too close to one another, which prevents one from observing them, especially if the density of experimental points on the temperature axis is not sufficient. On the other hand, a too strong field may drive the system too far from the critical point. The curves then become rather flat, which makes the estimation of the derivatives problematic. In addition, new terms not necessarily compatible with the scaling hypothesis may become important in the equation of state. The biasing field $E = 3 \times 10^6\ \mathrm{V\ m^{-1}}$ used to obtain figure 2 has been chosen so as to visualize the smooth and sharp inflection points. The curves of figure 2

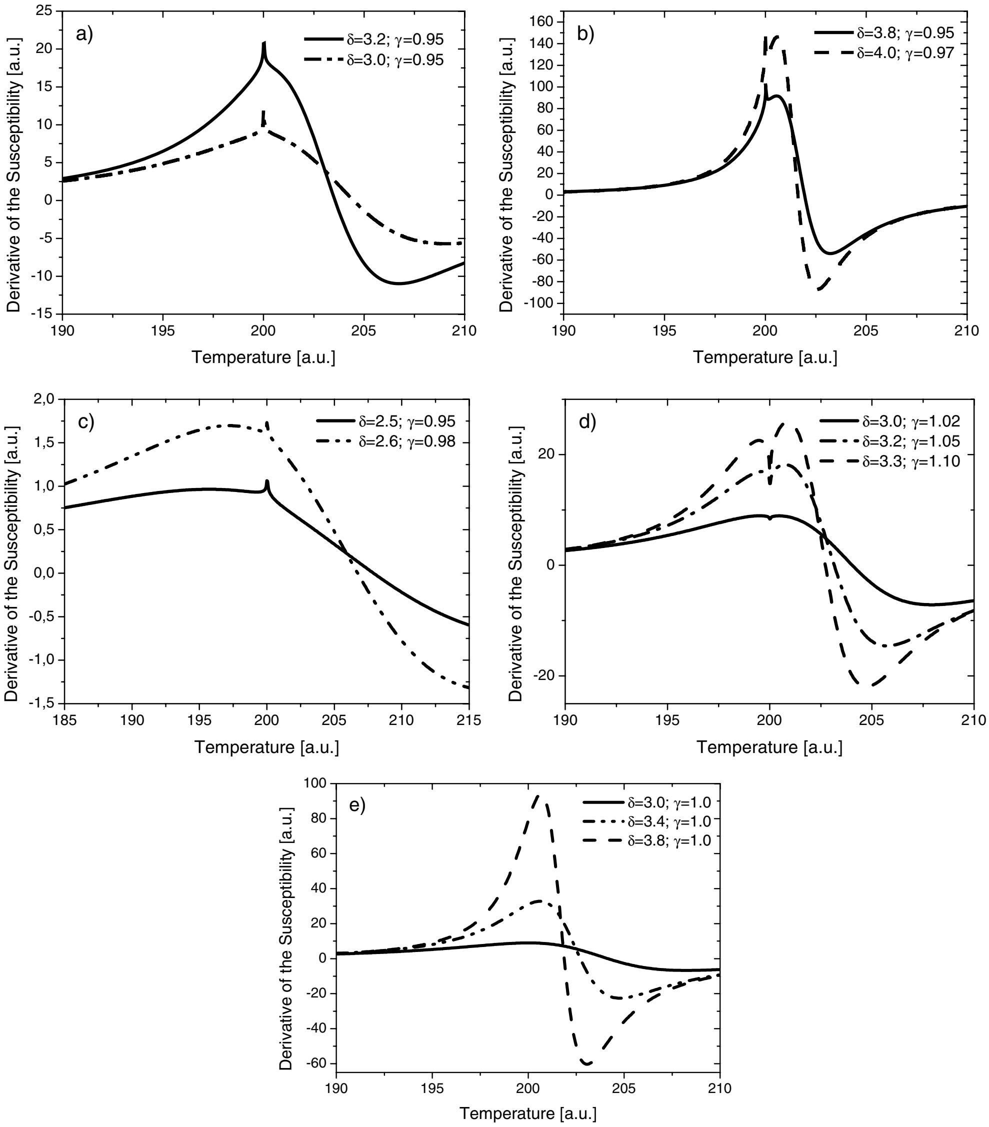

Figure 2. First derivative $\partial\chi/\partial\tau$ of the susceptibility in biasing field E for various values of the critical exponents γ and δ. The parameters a and b are identical for every curve and are equal to those from figure 1. The value of the biasing field is $E = 3 \times 10^6$ V m^{-1} and $T_C = 200$ a.u.

exhibit from two (figures 2(a) and (e)) to four extrema (figures 2(b)–(d)) corresponding to inflection points. The number and the shape of the extrema depend on the critical exponents γ and δ. For $\gamma < 1$ one can distinguish regions where the first derivative of the susceptibility has one minimum and one sharp maximum (see figure 2(a)) or where it has two minima and two maxima (one smooth and one sharp; see figures 2(b) and (c)). Figure 2(d) shows the case of $\gamma > 1$ and of any value of δ. Then there are two maxima and two minima, one of them being sharp or cusp-like. The sharp maximum or minimum occurs always at $\tau = 0$ for every field E. Therefore, this feature, once detected, may serve as a signature of the critical

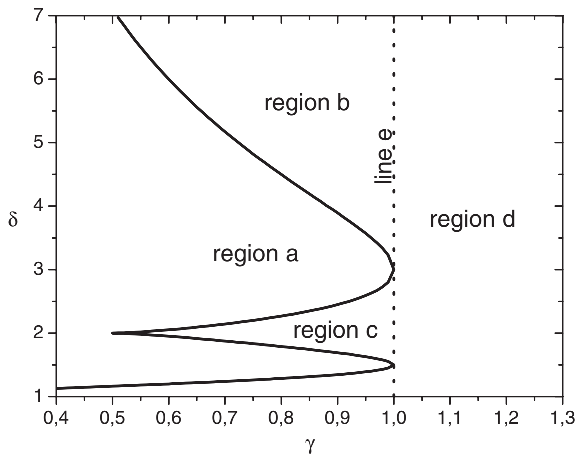

Figure 3. Regions of different sequences of inflection points of susceptibility curves in the (γ, δ) plane. Behaviours of first derivative $\partial\chi/\partial\tau$ in particular regions are: (a) as in figure 2(a), (b) as in figure 2(b), (c) as in figure 2(c), (d) as in figure 2(d), line (e) as in figure 2(e).

temperature. In figure 2(e) the first derivative of the susceptibility is shown for $\gamma = 1$ and for some values of the critical exponent δ. Only two smooth inflection points then are present. The practical application of the analysis of the derivative of the susceptibility to a specific material requires a precise knowledge of which of the situations illustrated in figures 2(a)–(e) really takes place. For example, one may easily overlook the cusp of figure 2(a), for some accuracy reasons. Nevertheless the experimental data may still comply with the corresponding values of γ and δ, if the position of this falsely smooth inflection point does not move on the temperature axis with E. This should be distinguished from the case of figure 2(e) or 2(c), where the temperature of the most discernable inflection point changes with the biasing field. To facilitate such an analysis we have constructed a diagram (figure 3) in which all the possible cases shown in figure 2 have been reported in the plane (γ, δ). This diagram is also useful if the critical exponents γ and δ are known from other studies and one wishes to check whether the measurements of the susceptibility in a biasing field confirm these results.

In conclusion, a non-classical value of γ manifests itself by three inflection points in the vicinity of T_C in addition to the unique inflection point to the right of the maximum. The sharp inflection point then is an indication of the critical temperature. The detection of a sharp inflection point is apparently conditioned by the appropriate choice of the biasing field and by the accuracy of the experiment.

3. Use of invariants in the determination of the scaling equation of state

The susceptibility $\chi(\tau, E)$ considered as a function of variables τ and E gives rise to some quantities which should be independent of the biasing field E provided that the scaling hypothesis is fulfilled. These quantities are called scaling invariants [8]. Generally, the invariants can be divided into two classes. The invariants in the first class depend on the actual value of the susceptibility (susceptibility value dependent invariants or SVD invariants), whereas those in the other class are independent of the value of the susceptibility (susceptibility value independent invariants or SVI invariants). Thus, the only piece of information needed to obtain the SVI invariants is the location of some features of the susceptibility curves (maxima

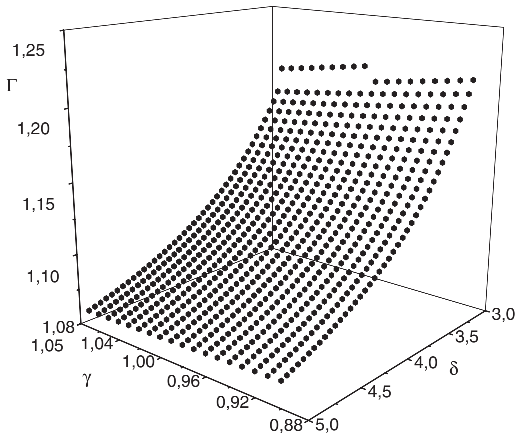

Figure 4. Invariant Γ, equation (6*b*), as a function of critical exponents (γ, δ) in the range of usually encountered values.

and inflection points) on the temperature axis, whereas the actual values of the susceptibility at these points then are immaterial. In what follows we present explicit expressions for invariants of both classes.

3.1. SVD invariants

The invariants that are dependent on the actual value of the susceptibility are represented here by the quantities Q and Γ. The invariant Q is defined in [8] as

$$Q = \frac{\chi(\tau_{\max}, E = 0)}{\chi(\tau_{\max}, E \neq 0)}, \tag{5a}$$

where $\tau_{\max} = T_{\max} - T_C$, and $T_{\max}$ is the temperature at which the susceptibility $\chi(\tau, E)$ has its maximum for the given value of the biasing field $E \neq 0$. The numerator of equation (5*a*) is taken at the same temperature but for $E = 0$. This invariant has been extensively studied by the authors and shown to depend on the critical exponent δ only [9, 12]:

$$Q = \frac{\delta - 1}{\delta - 2}. \tag{5b}$$

Also independent of E, a and b are the quantities

$$\Gamma = \frac{\chi(\tau_{\text{infl}}, E = 0)}{\chi(\tau_{\text{infl}}, E \neq 0)} \tag{6a}$$

where $\tau_{\text{infl}} = T_{\text{infl}} - T_C$, and T_{infl} is the temperature of an inflection point of the static susceptibility measured as a function of temperature at a non-zero biasing field E parallel to the ferroelectric axis. The explicit form of the invariant Γ for the equation of state given by equation (2) and for the rightmost inflection point, i.e. for the unique inflection point lying to the right of the maximum of the susceptibility (iprm) is

$$\Gamma = 1 - \delta + \frac{(\gamma + 1)(\delta - 1)^3}{\omega_{\text{iprm}}(\delta, \gamma)}, \tag{6b}$$

where $\omega_{\text{iprm}}(\delta, \gamma)$ is a known but complicated function, which depends only on the critical exponents δ and γ. The explicit form of $\omega_{\text{iprm}}(\delta, \gamma)$ is given in the appendix (equation (A.4)). Figure 4 shows the dependence of the invariant Γ on δ and γ. Analogous expressions can be given for the remaining smooth inflection points in the vicinity of the critical temperature. However, the analysis of these invariants with the use of experimental data may be difficult because of the proximity of the inflection points and of a possible sharp inflection point (see section 2).

3.2. SVI invariants

As example of the second class of invariants we will consider those which are related to the maximum and to the inflection points of the susceptibility curves:

$$\Omega = \frac{\tau_{\max}}{\tau_{\text{infl}}}. \tag{7}$$

The temperatures at which these features of the curves occur are the only parameters needed to determine the quantities Ω. In the present model one can build four invariants Ω_i for four inflection points $i = 1 \ldots 4$. The dependence of the temperature $\tau_{\max}$ of the maximum of the susceptibility on the field E is given by equation (4). The expression for the temperatures of the inflection points reads

$$\tau_{\text{infl}i} = \left(b^{1/\delta} a^{-1} \delta \frac{\omega_i(\delta,\gamma)(\rho_i(\delta,\gamma))^{-1/\delta}}{(\gamma+1)(\delta-1)^3} E^{\frac{\delta-1}{\delta}} \right)^{1/\gamma}, \tag{8}$$

where $\omega_i(\delta,\gamma)$ and $\rho_i(\delta,\gamma)$ are known functions given in the appendix (equations (A.1)–(A.3)). Inserting equations (4) and (8) into equation (7), one obtains the explicit formula for SVI invariants Ω_i:

$$\Omega_i = \left(\frac{(\gamma+1)(\delta-2)(\delta-1)^{2/\delta-1}}{\omega_i(\delta,\gamma)(\rho_i(\delta,\gamma))^{-1/\delta}} \right)^{1/\gamma}. \tag{9}$$

In contrast to the case of the invariants Q and Γ, the practical determination of the invariant Ω requires knowledge of the critical temperature T_C, because for example $\tau_{\max} = T_{\max} - T_C$.

4. Discussion

The proposed model based on the scaling function given by equation (2) is simple but at the same time non-analytical in the order parameter variable (polarization or magnetization). It allows one to determine the critical exponents δ and γ, and the critical temperature T_C, from measurement of the susceptibility in a biasing constant field conjugated to the order parameter. As has been shown in section 2, a non-classical value of the critical exponent γ should manifest itself by three inflection points in the vicinity of the critical temperature T_C. Moreover, the first derivative of the susceptibility $\partial\chi/\partial\tau$ exhibits a sharp maximum or minimum at the very critical temperature T_C for exponent γ different from unity. Therefore, this feature allows one to establish in a very straightforward way the value of the critical temperature T_C from measurements of the susceptibility χ as a function of the reduced temperature τ and the non-zero biasing field E. On the other hand, when the exponents γ and δ are known to follow the Landau theory, then the correctness of the equation of state (2) can be put into evidence by the field independence of the unique inflection point to the left of the maximum. This inflection point occurs exactly at the critical temperature T_C in this case. Readers may check this property for themselves by taking the NDE data for uniaxial ferroelectrics [4, 7–9, 11, 12]. The cited data show critical exponents close to, but not always exactly equal to, those predicted by the Landau theory. In particular, the exponent γ is often estimated as equal exactly to 1. The temperature of the unique inflection point obtained, for example, by taking the numerical derivative, will turn out to be independent of the biasing field. This feature has also been confirmed by the results obtained in our laboratory with different uniaxial ferroelectrics. The value of the biasing field E, used to measure the susceptibility χ, should be chosen so that the susceptibility curves are neither too steep (too weak fields) nor too flat (too strong fields). Too weak biasing fields do not separate the inflection points in the vicinity of the critical temperature T_C, which may lead to an incorrect interpretation of the experimental data of the susceptibility $\chi(\tau, E)$. On the other hand, too strong biasing fields E produce rather flat curves, so the inflection points are difficult to identify. Then the determination of the inflection points introduces a large error on the estimated values. The location of the inflection points on the temperature axis depends on the values of the critical exponents δ and γ, on the coefficients a, b and also on the field E, due to equations (8) and (A.1)–(A.3). The exponents δ and γ and also the coefficients a and b are constant quantities for given crystal. Only the value of the biasing field E is a quantity that changes in measurements. Therefore, the value of the measuring field E can be chosen such that the difference between inflection points near the critical temperature T_C is distinguishable in the experimental data.

The considered equation of state (2) gives rise to the scaling invariants presented in section 3. The invariants Q, Γ and Ω depend only on the critical exponents δ and γ, as follows from equations (5*b*), (6*b*) and (9). The set of the scaling invariants Q, Γ and Ω unambiguously defines the critical exponents β, γ and δ. Therefore, one can easily obtain the critical exponents γ and δ knowing the experimental values of the scaling invariants Q, Γ and Ω. The Widom equality [1, 10, 13] in the form $\gamma = \beta(\delta - 1)$ then allows one to calculate the critical exponent β. When the critical exponents β, γ and δ are known from other measurements then the calculated values can be compared with experimental ones. The non-isothermal conditions, history of the sample or too fast temperature variation in the measurements can affect the values of the susceptibility $\chi(\tau, E)$. When the differences between the calculated (on the basis of the scaling invariants) and experimental values of the critical exponents are beyond their errors one should reinvestigate the experimental data to check whether they really correspond to the isothermal equilibrium conditions. Therefore, the extent of these differences may indicate discrepancies between the theoretical isothermal susceptibility and the experimental susceptibility which can be adiabatic or partly adiabatic. Summing up, the presented scaling invariants Q, Γ and Ω are a useful tool permitting one to obtain the critical exponents when their values are not known from other measurements. Moreover, when the values of experimental scaling invariants show significant variation with the field E then this may indicate non-isothermal or non-equilibrium conditions of experiment.

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Appendix

The function $\omega_{\mathrm{iprm}}(\delta, \gamma)$ is obtained by equating to zero the second derivative of the susceptibility, $\partial^2\chi/\partial\tau^2 = 0$, given in equation (3). Then one gets a cubic equation in τ^γ. Solving this equation, one finds conditions for inflection points given by the formula (8) with

$$\omega_1(\delta, \gamma) = \tfrac{1}{3}\xi_1(\delta, \gamma) + 2\,\mathrm{sgn}(q(\delta, \gamma))\sqrt{\tfrac{1}{3}|p(\delta, \gamma)|}\cos\left(\tfrac{1}{3}\varphi\right), \tag{A.1}$$

$$\omega_2(\delta, \gamma) = \tfrac{1}{3}\xi_1(\delta, \gamma) - 2\,\mathrm{sgn}(q(\delta, \gamma))\sqrt{\tfrac{1}{3}|p(\delta, \gamma)|}\cos\left(60^\circ + \tfrac{1}{3}\varphi\right), \tag{A.2}$$

$$\omega_3(\delta,\gamma) = \tfrac{1}{3}\xi_1(\delta,\gamma) - 2\,\mathrm{sgn}(q(\delta,\gamma))\sqrt{\tfrac{1}{3}|p(\delta,\gamma)|}\cos(60^\circ - \tfrac{1}{3}\varphi) \tag{A.3}$$

where

$$\xi_1(\delta,\gamma) = \delta^2\gamma + 3\delta^2 - 6\delta\gamma - 7\delta + 4\gamma + 4,$$
$$\xi_2(\delta,\gamma) = \delta^2\gamma - 3\delta^2 + \delta\gamma + 8\delta - 4\gamma - 5,$$
$$p(\delta,\gamma) = \tfrac{1}{3}(\xi_1(\delta,\gamma))^2 + \xi_2(\delta,\gamma)(\gamma+1)(\delta-1)^2,$$
$$q(\delta,\gamma) = \tfrac{2}{27}(\xi_1(\delta,\gamma))^3 + \tfrac{1}{3}\xi_1(\delta,\gamma)\xi_2(\delta,\gamma)(\gamma+1)(\delta-1)^2 - (\gamma-1)(\delta-2)(\gamma+1)^2(\delta-1)^5,$$
$$\varphi = \arccos\left(\frac{3\sqrt{3}}{2}\frac{|q(\delta,\gamma)|}{|p(\delta,\gamma)|^{3/2}}\right)$$

and $\rho_i(\delta,\gamma) = 1 - \delta\frac{\omega_i(\delta,\gamma)}{(\gamma+1)(\delta-1)^3}$.

The inflection point to the right of the maximum is given by formula (8) with

$$\omega_{\mathrm{iprm}}(\delta,\gamma) = \begin{cases} \omega_1(\delta,\gamma) & \text{for } d(\delta,\gamma) \geqslant 0 \\ \max\{\omega_1(\delta,\gamma), \omega_3(\delta,\gamma)\} & \text{for } d(\delta,\gamma) < 0, \end{cases} \tag{A.4}$$

where $d(\delta,\gamma) = \frac{1}{4}(q(\delta,\gamma))^2 - \frac{1}{27}(p(\delta,\gamma))^3$.

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