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Absence of true critical exponents in relaxor ferroelectrics: the case for defect dynamics

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Abstract

It is argued that the large discrepancy ($\times 2$ in strontium barium niobate SBN) between experimental values from different kinds of experiment for the critical exponent β describing the temperature evolution of the order parameter in relaxors such as SBN arises from the fact that such ferroelectric systems, assumed to be [3D] random field Ising models by Kleemann *et al* (2002 *Europhys. Lett.* **57** 14), are not in thermal equilibrium. These arguments are illustrated primarily in SBN61—$Sr_xBa_{1-x}Nb_2O_6$:Ce with $x = 0.61$ and Ce = ca. 0.7%. An alternative model of Levanyuk and Sigov for defect-dominated dynamics is invoked. The inferred dimensionality of domain walls is also addressed, and the possibility of a $d = 5/2$ universality class controlled by domain dimensionality is considered as an alternative to defect dynamics; *inter alia*, four sets of $d = 5/2$ exponents (with $\beta = 1/2$, $1/3$, and $1/4$) satisfy all known scaling and hyperscaling equalities. The present results support the scepticism about SBN critical exponents emphasized by Chao *et al* (2005 *Phys. Rev.* B **72** 134105).

1. Introduction

Recently a series of papers dealing with critical (fluctuation-dominated) exponents in ferroelectrics has appeared. These emphasize two systems: (a) $SrTiO_3$ with O-18, for which we showed elsewhere that quantum criticality exponents are inappropriate to estimate the order parameter exponent β [1, 2]; and (b) the uniaxial relaxor ferroelectric strontium barium niobate, a tungsten bronze structure of formula $Sr_xBa_{1-x}Nb_2O_6$, usually grown for nonlinear optical device purposes with $x = 0.61$ and Ce doping (ca. 0.7%). The original studies of the temperature dependence of the order parameter (spontaneous polarization P) in this material and the related tungsten bronze $Ba_2NaNb_5O_{15}$ were by optical techniques [3–5], and for SBN:Ce yielded two independent values [6, 7] of $1–2\beta = 0.28$ (steady state) and 0.34 (transient)—hence $\beta = 0.36$ and 0.33, each with uncertainties of ± 0.02. It was suggested that these data were compatible with mean field behaviour near a tricritical point, which theoretically should yield $\beta = 1/4$ exactly at the tricritical point and $0.25 < \beta < 0.50$ on

the second-order side of the tricritical point. (A small applied field of $E = 0.32\,\mathrm{kV\,cm^{-1}}$ was required to reach the tricritical point exactly in $Ba_2NaNb_5O_{15}$.) Here β is defined as

$$P(T) = [(T_c - T)/T_c]^{\beta} = \tau^{-\beta}, \tag{1}$$

where T_c is the Curie temperature, which is also the transition temperature for a second order or tricritical ferroelectric transition; τ is reduced temperature.

The second, subsequent set of studies of critical exponents was carried out by more traditional electrical measurements [8–12], determining exponents β, γ and γ' [8], the latter characterizing electrical susceptibility as

$$\chi(T) = [(T - T_c)/T_c]^{-\gamma} = \tau^{-\gamma}, \tag{2}$$

where primes denote values below T_c and unprimed values above T_c. Thus we have two groups of research reports on the same critical exponents in the same material; however, these groups obtained conflicting values. A more complete set of exponents, having mean field tricritical values ($\alpha = 1/2$, $\beta \approx 1/4$, $\gamma = 1$, and $\delta = 5$) had been obtained [13–15] in the structurally related tungsten bronze $Ba_2NaNb_5O_{15}$ for α (specific heat exponent), β, γ and δ (dependence of P upon applied field E along the critical isotherm); these agreed with the β values in SBN from the same group. However, [8] obtained very different values for SBN: $\gamma = 1.85 \pm 0.05$, $\delta = 1.53 \pm 0.13$ and $\beta = 0.14 \pm 0.03$ near (but not very near—ca. 20 K) T_c. They interpreted their experimental results in terms of a [3D] random field Ising model (RFIM). We show below that their values strongly violate the Widom equation, expressed in scaling theory as an equality, and violate other scaling and hyperscaling equalities as well. This is a more serious criticism than the earlier observation by Fisher that RFIM violates the Josephson equation of hyperscaling [16].

2. Problems with critical exponents in random-field Ising models (RFIM)

Other authorities had previously pointed out 'the failure of "imperfect" scaling' in their theoretical treatment of systems with defects near phase transitions [17, 18] and that even the idea of true critical (fluctuation-dominated) exponents from random field Ising models below T_c is an oxymoron, because such systems are not in thermal equilibrium. Among other complications, relaxors such as SBN may exhibit nano-domain-like precursors 20 K above T_c, well into the paraelectric phases. Nano-domains can act as defects. Levanyuk and Sigov state in their text [17] regarding field-cooled measurements 'Thus the Ising system with defects of the random local field type (field-cooled state) is in fact a nonequilibrium one in the low temperature region of the non-symmetrical phase. Therefore it is hardly possible to interpret the critical behaviour of such systems in terms of critical indices found within equilibrium statistical mechanics'. This view is supported by other experts, including Blinc [19] and Salje [20].

The question then arises of whether the exponents fitted empirically in SBN are non-universal, and if they apply asymptotically as T approaches T_c. Other ferroelectric systems are well known in which a non-asymptotic point defect theory [17–23] gives exponents in good accord with experiments [24–27], but these exponents do not belong to a universality class, are not valid exactly at T_c, and do not need to satisfy any thermodynamic inequalities, such as those of Rushbrooke, Griffiths, etc [28–31]. A good example is the value $\alpha = 1.5$ in $SrTiO_3$ at 105 K [32, 33] or the values 2.2–5.7 for the exponent ζ describing ultrasonic attenuation and $\alpha \geqslant 1.0$ for specific heat in $BaMnF_4$, $KMnF_3$, or CsH_2PO_4 [34, 35]. Note that the anomalous part of the specific heat $\Delta C(T)$ is proportional to that of the sound velocity $\Delta v(T)$—(Janovec–Pippard relationship) [36, 37].

Earlier work on the changes in effective critical exponents due to spatial inhomogeneities in local electric polarization P (including those due to defects) was by Larkin, Pikin and Khmelnitskii [38–40], which forms the background for [17, 18]. In the present paper I consider both point defects [17, 18] and extended defects (including domain walls).

3. Reconciliation

3.1. Scaling

I show below that the values β and γ from Kleemann *et al* are implausible [8, 41, 42], and combined with their value of δ are incompatible with thermodynamic scaling.

First we note that the values $\gamma = 1.85 \pm 0.05$ and $\beta = 0.14 \pm 0.03$ given in [8–12, 41, 42] for SBN61 and attributed to a random field [3D] Ising model require an implausible value of $\delta \approx 13$ to satisfy the Widom equation as an equality (required by scaling theory); note that although $\delta = 15$ in the usual [2D] Ising model, it is $\delta = 5$ in [3D]:

$$\gamma' = \beta(\delta - 1); \tag{3}$$

but both of these values of δ strongly disagrees with the experimental value [9] of $\delta = 1.53 \pm 0.13$ and the theoretical value of $\delta = 1.8$ required [8] for a [3D] random field Ising model. This in itself, from static scaling, is sufficient to show that the [3D] RFIM values of δ, β, and γ from [8] are physically not self-consistent as true (thermal-equilibrium) critical exponents; below we show from hyperscaling that a value of $\eta < 0$ is required even if only β and γ are taken from [8], which is also implausible.

Their values of β and γ also require an equally implausible $\alpha' < 0$ to satisfy the Griffiths equation:

$$\alpha' + 2\beta + \gamma' = 2 \tag{4a}$$

as a scaling equality (note than in scaling theory $\alpha = \alpha'$ and $\gamma = \gamma'$). We emphasize that the values of β and γ from Kleemann *et al* [8–12] (even without their value $\delta = 1.53$, which prohibits *any* solutions satisfying static scaling) inserted into (4) yield

$$\alpha' = -0.13 \pm 0.06. \tag{4b}$$

The negative value of α' would be unique among ferroelectrics. As one possible route to reconciling these values, we note that $\gamma' = 5/2$ in the defect theory [17, 18], so that as T_c is approached γ' varies from 1 (mean field) to 2.5; it is not unreasonable that the reported [8] value of ca. 1.85 (at 350 K) or even >2 could be inferred over a region of T near T_c. In this context it is important to point out that Kleemann *et al* actually measured [8] $\gamma = 2.1$ below $T = 350$ K ($T_c = 320$ K), not 1.85, and that this value is close to the defect predictions of 2.5; they interpreted this as due to domain wall contributions (a kind of defect) and thereby justified values greater than the 1.97 predicted by RFIM. Kleemann *et al* refer [8] to their value of $\gamma = 2.1$ as 'unreasonably large', yet we see that it is quite close to (and smaller than) the defect model prediction of 2.5. Similarly, the specific heat exponent α in the defect-dominated regime is theoretically 1.0–1.5, which has been previously observed but misinterpreted in both CsH_2PO_4 and $KMnF_3$ [34, 35]; see [26]. In some crystals, such as ferroelectric $BaMnF_4$, it is easy to discriminate between the defect regime below the transition temperature (due to antiphase boundaries APBs in incommensurate $BaMnF_4$), where $\alpha' = 1.1 \pm 0.1$, and the mean-field tricritical regime (defect-free) above T_c where the APBs disappear and hence $\alpha = 0.54 \pm 0.05$ [27].

3.2. Hyperscaling

Unlike scaling theory, hyperscaling explicitly involves the dimensionality of the system and consequently other critical exponents. We showed recently [1] that hyperscaling requires as an equality

$$\gamma' - 2\beta = \nu[4 - d - 2\eta], \tag{5}$$

where ν is the critical exponent in the correlation function and η, that in the structure factor $S(q)$. The standard [2D] Ising model has $\gamma' = \gamma = 7/4$; $\beta = 1/8$; $\nu = \nu' = 1$; and $\eta = 1/4$; these values satisfy (5). If we consider

$$\gamma = (2 - \eta)\nu \tag{6}$$

which is equation (12.29) of Stanley's text [30] and equation (5.4.10) of the text by Chaikin and Lubensky [31] and also

$$d - 2 + \eta = 2\beta/\nu, \tag{7}$$

which is equation (12.28) in Stanley and equation (5.4.15) in Chaikin and Lubensky, we find from (6) and (7) for $d = 3$ that the experimental values of β and γ from [8] yield a single solution: $\nu = 0.7$ and $\eta = -0.6$ ($\nu = 0.7$ is very plausible and indeed 0.68 was obtained experimentally [33] for thin surface layers of $SrTiO_3$; but $\eta = -0.6$ is an implausible value, since $\eta > 0$ for all solvable exact models and $\eta < 0$ would cause an problems for the structure factor $S(q)$ and its Fourier transform, the pair correlation function $G(r, \tau)$). One problem with $\eta < 0$ is the Buckingham–Gunton inequality $d(\delta - 1)/(\delta + 1) \geqslant 2 - \eta$, which rigorously requires for $d = 3$ that $\delta \leqslant 5$ (typical for [3D] models and inclusive of the 1.8 in RFIM) implies $\eta > 0$. Hence, even ignoring the value [8] of $\delta = 1.55$, the values of β and γ alone from [8] for $d = 3$ violate hyperscaling [16].

The exponent η is defined as the wavevector dependence of the correlation function

$$G(\tau, q) = G_0 q^{-2+\eta}. \tag{8}$$

Fisher [43–45] has discussed the fact that η is not negative ($0 \leqslant \eta \leqslant 2$), more readily seen by Fourier transforming it to $G(r, \tau)$. For lattice gas models η is one-quarter in [2D] and one-16th in [3D], and for fluids experimentally $0 < \eta \leqslant 0.2$.

Therefore, since $\delta = 1.8, \beta = 0.15$ and $\gamma = 1.85$ fail to satisfy the scaling equations (and parenthetically also $\eta < 0$ is required), we have in equations (4)–(8) a *reductio ad absurdum* proof that the SBN critical exponents of Kleemann *et al* [8] cannot satisfy random field Ising models and scaling for the claimed [3D] dimensionality. This suggests that the correct explanation may lie in models, such as the Levanyuk–Sigov defect model, which do not need to satisfy scaling or thermodynamic inequalities (since they are not asymptotically valid as $T \Rightarrow T_c$). And it is compatible with the *caveat* from Levanyuk and Sigov that experimental field-cooled values cannot be compared with those of equilibrium statistical mechanical models, since the former are not in thermal equilibrium.

3.3. Thermal focusing experiments [3–5]

3.3.1. Dependence upon β. It is important to emphasize that the temperature dependence of the diameter of the transmitted beam in the thermal focusing experiments on SBN varies, assuming a Kerr-like effect on the index of refraction n, $\Delta n = mP^2$ (proportional to the square of the polarization), as $\tau^{2\beta-1}$ [5, 6], only if any divergence in thermal conductivity κ is negligible. Although this usually appears to be the case in ferroelectrics, data are rarely published for $\kappa(T)$ near T_c. If $\beta = 1/2$ (mean field second-order transition), there is no exponential temperature dependence at all ($2\beta - 1 = 0$), often manifest as a step discontinuity

or a logarithmic divergence. This is readily ruled out by all experiments on SBN. Similarly β cannot be $>1/2$, or the diffraction ring diameter would decrease as T_c is approached, rather than increase. Both the quasistatic thermal focusing measurements and the dynamic transients yield, independently [3–5], values of $\beta = 0.33$–0.36. These empirical exponents satisfy the data over a wide temperature range—of order 20 K. This in itself militates against a true critical (fluctuation-dominated) regime, according to the Ginzburg criterion, whereas [17] (p 75) calculates that the defect model will dominate displacive systems between ca. 2 K and a few tens of degrees from T_c. By comparison, Kleemann originally published [41] $\beta = 0.06$ and then subsequently, from Zalar and Blinc [42], $\beta = 0.15$. The latter value is from NMR, but the Ljubljana authors have privately suggested [20] that the transition might be slightly first order, i.e. near a tricritical point, so that their apparent sharp increase (and hence small exponent) may be due to a small discontinuity (we note parenthetically that the relaxor lead magnesium niobate–lead titanate PMN-PT also has a slightly first-order transition [46, 47]). Kleemann *et al* reported an order parameter relaxation time of 3.5 ms, which is in the same range as the 16 ms thermal relaxation time reported by O'Sullivan *et al* [48]. This may result in coupling between order parameter fluctuations and entropy fluctuations, complicating any effective exponent. Values of β of order 0.15 are totally incompatible with the thermal focusing data. This suggests that the two kinds of experiments may not both be measuring the same β; i.e., there may be empirical exponents here that arise from extrinsic causes. We note that in the presence of visible light, Gao *et al* have also shown [49–52] that $Ce^{3+} + Nb^{5+} \Rightarrow Ce^{4+} + Nb^{4+}$ charge transfer occurs in SBN:Ce on the same timescale (milliseconds) as the thermal relaxation and order parameter relaxation. This is a possible explanation for why β differs in optical measurements (strong visible light) and electrical measurements (in the dark or subdued room light). $Ce^{3+} \Rightarrow Ce^{4+}$ may additionally complicate any dynamics near T_c, since the ionic radii differ, and further suggests defect models.

3.3.2. Inclusion of divergence in thermal conductivity κ in thermal focusing data. The angular diameter $\theta(T)$ of the slightly elliptical beam (outer ring) in thermal lensing is given for light polarized along x and propagating along $i = y$ or z by

$$\theta_i(T) \approx (\mathrm{d}n_x/\mathrm{d}T)/\kappa_{ii}(T), \tag{9a}$$

where κ is the thermal conductivity tensor ($i = y, z$) and n, the index of refraction. Near T_c [6, 53], suppressing subscripts,

$$(\mathrm{d}n/\mathrm{d}T)/\kappa(T) \approx [\tau^{2\beta-1}/(\kappa(0) + \Delta\kappa\tau^{-a})], \tag{9b}$$

i.e., $\kappa(T)$ varies as $\kappa(0) + \Delta\kappa(T)$, with $\Delta\kappa(T)$ diverging weakly and becoming more anisotropic as T approaches T_c. For liquids the transport properties, especially thermal conductivity, are treated by mode–mode coupling theory. Unfortunately this approach yields different exponents in different frequency regimes. Moreover, this model has not generally been used to treat solids. In both SBN:Ce and $Ba_2NaNb_5O_{15}$ the thermal conductivity is noticeably anisotropic near T_c ([3] Chen *et al*, 1991; figure 8), so $\Delta\kappa_{ij}$ definitely has a measurable effect; however, existing data from Xi *et al* [54, 55] suggest that it diverges only weakly near T_c in ferroelectrics, so that $\Delta\kappa(T)$ is only a small correction, which can be of either sign (negative in $LiNbO_3$ but positive in $KLiSO_4$), usually a decrease in κ of ca. 10–20% [55].

3.3.3. Use of the spherical aberration threshold [56, 57]. We can also estimate the maximum increase [55] in $\Delta\kappa$ at T_c as $<50\%$ of $\kappa(300\ \mathrm{K})$ by means of an equation for the onset of spherical aberration in a thermal lens [56]:

$$P(\text{threshold power}) = 1.6\lambda\kappa(T)T/(bL\mathrm{d}n/\mathrm{d}T), \tag{10}$$

where λ is wavelength (514 nm); L, beam length in the sample (ca. 3 mm); b, absorption coefficient (ca. 0.26 cm^{-1}); dn/dT is the change in refractive index with temperature and is of order 10^{-5}–10^{-4} K^{-1} near T_c. This equation predicts an aberration threshold at 200 mW for our collimated laser beam of ca. 20 μm, using $\kappa(300\ K) = 5.9\ W\ K^{-1}\ m^{-1}$ [54], whereas the measured threshold value [4] was 300 ± 20 mW. Therefore corrections for divergence in $\kappa(T)$ are unnecessary, because the inferred value [55] of $\kappa(T_c)$ differs by $\leqslant 50\%$ from $\kappa(300\ K)$; i.e., in (3)–(5), (13), $\kappa(T) \gg \Delta\kappa(T)$. As a semi-qualitative estimate, inclusion of an increase in $\kappa(T)$ of order 50% at T_c in either $Ba_2NaNb_5O_{15}$ or SBN will decrease slightly the inferred value of β in the thermal focusing experiments from the reported values of 0.33–0.36 to nearer 0.25, compatible with a mean field tricritical model. Asymptotically $\Delta\kappa(T)$ probably varies as $\tau^{-2/3}$ [58–60], i.e. in (9*b*) $a = 2/3$. Thus, very close to T_c, the beam divergence might vary as $\tau^{2\beta-1/3}$; however, there is no evidence for this regime, where θ would actually *decrease* as T approached T_c, in the experiments [3–5], which typically did not probe $T_c - T < 1$ K. Nor is there any evidence that $\Delta\kappa > \kappa(300\ K)$: the divergence in thermal conductivity $\kappa(T_c)$ is $< 1/2\kappa(300\ K)$ and hence negligible to a first approximation. The absorption coefficient b is observed not to be singular at T_c. Since it arises from thermal fluctuations near the Curie temperature, the change in thermal conductivity can be quenched via a small field E of a few kV cm^{-1} [55].

3.4. Predictions

3.4.1. Specific heat and ultrasonic attenuation. The models discussed above are readily falsifiable. The defect model predicts that the T-dependence of the specific heat will scale with an effective exponent $\alpha(\text{def}) = 2 - \nu$, which in the mean field is 1.5 and for the defect $\nu = 1$ is 1.0; and the ultrasonic attenuation exponent is $\zeta(\text{def}) = 5\nu$, which in the mean field is 2.5 and for the defect $\nu = 1$ is 5.0 (these values, both for α and ζ, have been found in other ferroelectrics [26, 32–35, 61, 62]). These predictions should be checked for SBN. Note that intrinsic mode–mode coupling theory gives [58, 59] quite different values of $\zeta = 1.0$ (Heisenberg antiferromagnets or superfluids) to 1.33 (single-axis ferro- or anti-ferromagnets) for ζ, about half the predicted defect minimum value of 2.5; this large ratio should make it easy to discriminate between the two models. (The thermal focusing experiments yield $\beta = 0.3$, incompatible with the data of Zalar even when the weak divergence in thermal conductivity is included, and suggesting a mean field tricritical point; but such data are not capable of yielding γ, α, or ζ.)

Defects can also theoretically produce other measurable experimental anomalies in ferroelectrics, such as antisymmetric stress tensors, local rotations, and hence asymmetric elastic coefficients $C_{ij} \neq C_{ji}$ [63, 64], found experimentally. These are often non-equilibrium and have net internal stresses and torques [25].

3.4.2. Other defect exponents: δ, ν, and η. One should consider the defect model predictions for critical exponent δ, which characterizes the dependence of the order parameter P on an applied conjugate field E along the critical isotherm T_c. Levanyuk and Sigov [17] do not discuss this exponent, but their equations (p 72 of [17]) yield $\delta = 2$. Experimentally, this would be difficult to distinguish from the RFIM prediction of 1.8 (and [8] reports a compatible $\delta = 1.53 \pm 0.15$). For barium sodium niobate, thermal focusing yielded a mean-field value of $\delta = 5.0$–5.1 [13], but no measurements were made on SBN in an applied field E. These experiments are difficult; in materials with finite conduction it is difficult to vary field E without changing temperature T away from the critical isotherm. Similarly, the prediction [17] for β is that it is slightly reduced from mean field: $\beta < 1/2$ (p 74, [17]), which we express as 0.3–0.4 in table 1. For the correlation length exponent η, Levanyuk and Sigov [17] show (p 104) that the

Table 1. Empirical parameters for dimension $d = 2.5$. (Possible critical exponents (conventional notation) satisfying scaling and hyperscaling theory equalities for fractional dimension $d = 5/2$ (these sets are not unique and were derived for sets 1 and 2 assuming $\nu = 1$ as in the [2D] Ising model; for set 3 by trying $\nu \approx 2/3$ as in [3D] Ising or Heisenberg models); for set 4, $\nu = 1/2$, as in the mean field. The Levanyuk–Sigov defect model results [17] are shown for comparison; these are non-asymptotic at T_c and need not satisfy any thermodynamic (in)equalities (11)–(19), including the dynamical ones[a,b,c] for ultrasonic attenuation, quasielastic scattering intensity, or thermal diffusion.)

Parameter (for $d = 5/2$)	Value (Set 1) [2D]-Ising-like	(Set 2) [2D]-Ising-like	(Set 3) [3D]-Ising-like	(Set 4) Mean-field-like	Defect model
			Statics		
Specific heat	$\alpha = -1/2$	$\alpha = -1/2$	$\alpha = 1/3$	$\alpha = 3/4$	$\alpha = 3/2$
Order parameter	$\beta = 1/2$	$\beta = 1/4$	$\beta = 1/3$	$\beta = 1/4$	$\beta \approx 0.3$–0.4
Susceptibility	$\gamma = 3/2$	$\gamma = 2$	$\gamma = 1$	$\gamma = 3/4$	$\gamma = 5/2$
Critical isotherm	$\delta = 4$	$\delta = 9$	$\delta = 4$	$\delta = 4$	$\delta = 2$
Correlation length	$\nu = 1$	$\nu = 1$	$\nu = 2/3$	$\nu = 1/2$	$\nu = 1$
Pair correlation	$\eta = 1/2$	$\eta = 0$	$\eta = 1/2$	$\eta = 1/2$	$\eta = -2$
			Dynamics		
Ultrasonic attenuation[a] $\zeta = 2\nu - \gamma + \alpha/2$	$\zeta = 1/4$	$\zeta = -1/4$	$\zeta = 1/2$	$\zeta = 3/2$	$\zeta = 5\nu = 2.5$–5.0
Landau–Placzek ratio (Rayleigh/Brillouin) $\psi = \gamma - \alpha$	$\psi = 2$	$\psi = 5/2$	$\psi = 2/3$	$\psi = 1/4$	$\psi = 2$
Thermal diffusivity[b] $\Lambda = \gamma - \nu$	$\Lambda = 1/2$	$\Lambda = 1$	$\Lambda = 1/3$	$\Lambda = 1/2$	$\Lambda = 3/2$[c]

[a] $\zeta = 1$ or $4/3$ in intrinsic mode–mode coupling theory [30, 31].
[b] Typically Λ diverges as $\tau^{\nu-\gamma} = \tau^{-2/3}$ in fluids [30, 31, 58, 59].
[c] Change in kinetic coefficient ([17], p 93) due to coupling of the order parameter with local temperature fluctuations.

x-ray scattering intensity $I(\tau) = c(A\tau + fq^2)^{-2}$, rather than the usual $I(\tau) = c(A\tau + fq^2)^{-1}$. At T_c this implies $I(q)$ varies as q^{-4}. Since η is defined as $I(T_c) = q^{-2+\eta}$, this implies a defect $\eta = -2$. Note that this does not satisfy hyperscaling and indeed the defect theory is asymptotically invalid at T_c. This contribution to x-ray intensities should be important only near T_c, but [17] estimates its detection level as within $T_c/100 =$ ca. 3 K, an experimentally accessible regime. The exponent ν differs for different symmetries of defects in the Levanyuk–Sigov theory (p 57) and is $\nu = 1$ (Ising-like) for the simplest case of a dipole-like defect.

4. Domain wall dimensionality: the case for $d = 2.5$ Hausdorff dimension

As an alternative to the defect-dynamics model considered above, I can suggest a second possible way of reconciling experiments and unusual exponents with theory by considering the possibility that the dimensionality of ferroelectric transitions may be $d = 2.5$. Fractional dimensionalities are not thermodynamically unphysical, although we note that Huse and Fisher discuss [65] what they term the 'unphysical dimensionality range $2 < d < 3$' in their treatment of pair correlation functions for random field systems. This approach is not unrelated to the defect mechanisms I discuss above, because the motivation is that domain walls in ferroelectrics have dimension $D_d = 2.5$, and these walls are a kind of extended defect that may influence or even control dynamical behaviour near T_c. I emphasize that the parameters given below are purely empirical and are not the solutions of any microscopic model, such as an Ising model in dimension 2.5.

4.1. Why is d not 1.5?

The domain wall dimensionality D_d relates to other critical exponents evaluated experimentally. Kleemann *et al* [66] have recently given an effective dimensionality of ferroelectric domain walls of $D_d = 1.5$ in a three-dimensional system. A flat wall in a two-dimensional system has $D_d = 1$, so $D_d = 1.5$ is plausible for [2D] systems; however, in three-dimensional systems $D_d \geqslant 2$. $D_d = 1.5$ conflicts with the value of $D_d = 2.5$ measured by Paruch *et al* [67] and with the roughening observed [68, 69] in other three-dimensional systems. True Hausdorff dimensions of $D_d < 2$ for domain walls in [3D] systems seem physically implausible. It is possible that the domain dimensionality dominates dynamics in ferroelectrics near T_c and hence that a correct description of critical behaviour in ferroelectrics will require calculations for dimensionality 2.5; to our knowledge this has not been done. I note parenthetically, however [68], that there is always uncorrelated noise in the slow scan axis of an AFM microscope which can under some circumstances give a spurious Hausdorff dimension of 2.5; but this does not seem to be applicable for the length scales (>100 nm) examined by Paruch *et al*.

If we look at Fisher's modifications [43–45] of the Ornstein–Zernike theory, we find that for $d = 2$, the theory fails, as is well known (the prediction is that the correlation function $G(r, T_c)$ *increases* with distance r). However, for $d > 2$, including fractional d, $G(r, T_c) \approx ar^{(2-d)}$ [65] and η is still defined as $G(r, T_c) = ar^{(2-d-\eta)}$ for $d = 5/2$. In practice, for [3D] systems, this implies $G(r)$ varies very slightly faster than r^{-1} (since experimentally $\eta =$ ca. 0.04, at least for fluids). If we naively insert $d = D_d = 5/2$ from Paruch *et al* into this Ornstein–Zernike formalism, we find that η is not unphysical, and in fact yields a spherical fluctuation droplet in the Huse–Fisher random field model with $G(r, T_c) \approx ar^{-1/2}$. In the original Ornstein–Zernike model, $\nu = 1 = \gamma/2$ (which satisfies hyperscaling equation (6). Therefore a second approach, alternative to defect dynamics, to the apparent failure of experimental ferroelectric critical exponents to satisfy hyperscaling might lie in the possibility of a $d = 5/2$ universality class, controlled by domain dimensionality, and heretofore unexplored. For example, for $d = 5/2$ equations (6), (7) are satisfied *inter alia* by $\gamma = 3/2$, $\nu = 1$, $\eta = 1/2$; and table 1 gives a complete (non-unique) parameter set satisfying as equalities all of the applicable scaling and hyperscaling relationships given by Griffiths [29] or Stanley ([30] p 61). The value of $\delta = 4$ is particularly interesting, because it violates the conjecture in the past that δ is an odd integer for all analytically solvable models (e.g., 3 for second-order mean field; 5 for tricritical mean field, Ornstein–Zernike, spherical model, [3D] Ising, and [3D] Heisenberg; or 15 for [2D]-Ising). The values in table 1 are not incompatible with some of the experiments reported on SBN or BNN ($Ba_2NaNb_5O_{15}$), although these ferroelectric transitions are probably tricritical, with in mean field $\beta = 1/4$, rather than $1/2$; a second empirical set compatible with this value is also given in table 1. These values form a set of purely empirical exponents resembling second-order mean field and tricritical mean field with respect to order parameter exponent β, and were motivated by my assuming $\nu = 1$, as in the [2D] Ising model or the Ornstein–Zernike theory and/or $\beta = 1/4$ or $1/2$. Note that my values of η all satisfy Fisher's additional and relatively obscure requirement [43–45] that $\eta \leqslant (2 - d/3)$, which is 1.17 for $d = 5/2$. Of course the caveat about comparing field-cooled data with equilibrium thermodynamics discussed in section 2 above still requires careful consideration for such a $d = 5/2$ 'critical' treatment.

4.2. Scaling equalities in d = 2.5 dimensions

All four $d = 5/2$ sets of exponents in table 1 satisfy the following thermodynamic inequalities as exact scaling equalities, as well as the three hyperscaling equalities (5)–(7). These equations

are not all independent, so in general there are infinitely many solutions. The second set resembles experimental values in SBN (equations below assume exponents below T_c are equal to those above, a static scaling assumption). *Mathematica* shows that all solutions for $\nu = 1$ require the relationship $\beta = 1/4 + \eta/2$. If we require $0 < \beta < 2/3$, this implies that there are only these two solutions with integer or half-integer η, viz. $\eta = 0$ or $1/2$. Note that equations (5)–(7) and (11)–(19) actually contain only five independent (nonlinear) equations in seven unknowns ($\alpha, \beta, \gamma, \delta, \nu, \eta, d$); therefore, the set of solutions is infinite unless other physical constraints are added: I included the four constraints $\gamma \geqslant 1$, $0 < \beta \leqslant 2/3$, $\nu > 0$, and $\delta \geqslant 1$, but not the Fisher constraint $0 \leqslant \eta \leqslant (2 - d/3)$, which is however satisfied for all sets. I emphasize that these sets need not correspond to any physical model; they are merely empirical parameters that do not violate scaling or hyperscaling. The constraint $\beta \leqslant 2/3$ follows the Heisenberg limit of $\beta = 0.65$ from Sheng and Salamon [71] or Bastie *et al* at tricritical points [72].

Buckingham–Gunton	$d(\delta - 1)/(\delta + 1) = 2 - \eta$	(11)
Rushbrooke I	$d\gamma/(2 - \alpha) = 2 - \eta$	(12)
Rushbrooke II	$\alpha + 2\beta + \gamma = 2$	(13)
Fisher	$(2 - \eta)\nu = \gamma$	(14)
Josephson	$d\nu = 2 - \alpha$	(15)
Griffiths I	$\alpha + \beta(1 + \delta) = 2$	(16)
Griffiths II	$\gamma(\delta + 1) = (2 - \alpha)(\delta - 1)$	(17)
Widom	$\gamma = \beta(\delta - 1)$	(18)
Stanley	$\beta(2 - \alpha + \gamma) = (2 - \alpha - \beta)(2 - \alpha - \gamma).$	(19)

4.2.1. Fractional dimension $d = 2.5$ solutions with 'classical' $\nu = 1/2$ values. For $d = 2.5$ and a mean-field-like exponent $\nu = 1/2$, the Josephson equation (15) yields $\alpha = 3/4$. Constraining the equations above to $d = 5/2$, $\alpha = 3/4$, and $\nu = 1/2$ yields an infinite number of solutions, of which the only one with half-integer values is $\eta = 1/2$, $\beta = 1/4$, $\delta = 4$, and $\gamma = 3/4$, shown as set 4 in table 1. This resembles the mean-field tricritical solution, with which it shares values of β, ν, and γ.

4.2.2. Fractional dimension $d = 2.5$ solutions with $\nu \approx 2/3$. The [3D] Ising and Heisenberg models both have $\nu \approx 0.64$–0.70. Therefore it is useful to look for [3D]-like solutions for $d = 2.5$ to compare with the [2D]-Ising-like solutions in table 1. I find that at least one solution does exist with $\nu \approx 2/3$ and moreover that it has $\beta \approx 1/3$, as in the [3D] Ising ($\beta \approx 5/16 = 0.3125$) or [3D] Heisenberg model ($\beta \approx 0.345$); this is set 3 in table 1.

4.2.3. Comments on dynamic parameters in table 1. In the mean field $\zeta = 5/2$; for $\nu = 1$, $\zeta = 5$. ζ is often 'large' experimentally: $\zeta = 2.2 \pm 0.3 \approx 5/2$ for the longitudinal mode in $BaMnF_4$ experiments, and for the transverse modes, $\zeta = 3.9 \pm 0.1$ and 5.7 ± 0.3 [61, 62]. In each case there is better agreement with defect theory than with $\zeta = 1$ or $4/3$ from fluctuation (critical) theory. The fact that transverse and longitudinal modes have different defect responses is explained by Yermolov *et al* [73, 74].

Experimental values for the Landau–Placzek ratio for ferroelectric KH_2PO_4 are $\psi = 1.5 \pm 0.2$ and are attributed to defects [75]; for ferroelectric $KH_3(SeO_3)_2$ with deuterium defects unambiguously identified as responsible, $\psi = 0.95 \pm 0.05$ [76]; and for ferroelectric lead germanate $\psi = 1.0 \pm 0.2$ [77]. For fluids, these are also about 1.0: experimentally

$\psi = 0.95 \pm 0.15$ [78] and 1.02 ± 0.03 [79]; and the theoretical intrinsic fluid value is 1.06 ± 0.05 [80].

Both thermal and electrical conductivity change at T_c [81]. The *electrical* resistivity diverges near T_c due to both soft mode scattering [82] and defects [83].

5. Conclusions

The fitting of critical exponents for SBN [6] to a [3D] random field Ising model violates static scaling relationships (e.g., the Widom equation) for the claimed values of β, γ, δ; and even the values of β and γ alone, without δ, violate hyperscaling for η (yielding $\eta < 0$, which according to Fisher [43–45] is unphysical). $\beta = 0.15$ is also incompatible with optical data for β [3–5]. Evaluation of critical exponents is moreover not justified for field-cooled data because these are not in thermal equilibrium [17, 18]. The suggested reconciliation is that the SBN data are dominated by defect dynamics [17, 18, 22, 23], perhaps involving the Ce doping. The Levanyuk–Sigov defect model predicts $\delta = 2$, $\beta \leqslant 0.5$, $\gamma = 2.5$, which are not in complete disagreement with the SBN experimental values of $\delta = 1.53 \pm 0.15$ and $\gamma = 1.85$–2.1 from Kleemann *et al* [8], and $\beta = 0.3$ from Scott *et al* [3–5].

An alternative possibility is that a new universality class with fractional dimensionality $5/2$, corresponding to the domain dimensionality, might be invoked; I give four empirical sets of values for the common critical exponents which satisfy scaling and hyperscaling equalities for this case, as well as satisfying the Fisher relationship $\eta < (2-d/3)$. These arguments about defect dynamics or fractional dimensionality are not wholly unrelated, because it is supposed that any fractional dimensionality present might arise from the dimensionality of the domain walls, which are themselves a kind of extended defect. My conclusions about inapplicability of RFIM critical exponents in SBN are strongly supported by the recent pyroelectric polarization studies of Chao *et al* [84, 85], which disagree with the results of Kleemann *et al* [8], and who conclude '... one needs to use great caution in interpreting the details of the T-dependent polarization in terms of critical phenomena' in this material, and stress that uniaxial SBN is very unlike the pseudo-cubic relaxors of the PMN (lead magnesium niobate) family. Note that the long tail and detailed shape measured by Chao *et al* for the order parameter versus T above T_c strongly resemble that in figure 7.2 from [17]; this is analogous to the temperature dependence of magnetization $M_k(T)$ for a ferromagnet in an applied conjugate field H_k.

Finally, table 1 includes a listing in conventional notation of all the non-universal 'critical' exponents from the Levanyuk–Sigov defect theory; readers of [17] will find that this was not a trivial chore.

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