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1989 J. Phys. A: Math. Gen. 22 593

(http://iopscience.iop.org/0305-4470/22/6/012)

J. Phys. A: Math. Gen. **22** (1989) 593-609. Printed in the UK

Bivariate statistical analysis of data near a critical point: the case of the singular behaviour of the electrical resistivity temperature derivative

M Ausloos†

Institut de Physique B5, Université de Liège, B-4000 Liège, Belgium

Received 13 June 1988

Abstract. A (bivariate) anisotropic metric is used to fit theoretical expressions of the electrical resistivity temperature derivative near a critical point. Data chosen are those on TbZn. Effects of temperature and voltage measurement error (or precision) are investigated. Critical amplitudes, the critical exponent and the critical temperature are greatly affected by small uncertainties. The necessity to report such data uncertainties is emphasised. No definite conclusion on parameter values can be made at this time. A method of 'randomly modified data' shows the complementarity between simulation and laboratory work. The method *a posteriori* indicates how one may observe variations in *assumed* 'constant errors' for standard measurements.

1. Introduction

In modern statistical mechanics, critical exponents are key parameters in deciding upon the type of phase transition occurring in systems (Fisher 1967, Kadanoff *et al* 1968). Theoretical predictions of such parameters are now mainly based on the renormalisation group technique (Ma 1973, 1976, Fisher 1974, Wilson 1983 and references therein).

Much experimental work has been performed near phase transitions in homogeneous and inhomogeneous systems, often resulting in extraction of critical exponents. Although much work is still needed, one might state that the behaviour of static properties is quite well understood in most systems. Many models and much intuition have been available to explain most of the known anomalies (i.e. critical exponents), including crossover effects, dimensionality effects, etc. The theory of 'critical exponents', the scaling hypothesis and universality laws are thus quite well established for static properties (Fisher 1967, Stanley 1971, Ma 1976).

The case of time-dependent or non-equilibrium properties is not so well established. Non-universal laws are predicted, and critical exponents are not so easily calculated (through dynamic renormalisation group or other techniques). Relations between 'static and 'dynamic' critical exponents are not obvious either—nor is it known whether indeed they exist!

On the other hand, good experimental conditions are crucial. It is well known that experimental data in the vicinity of a phase transition must be taken with great care due to the importance of large fluctuations and their subsequent (theoretically infinite)

† E-mail address: U2150 MA at BLIULG11 (EARN).

0305-4470/89/060593+17$02.50

correlation length, more so when dealing with non-equilibrium properties, i.e. where a gradient is present. Experimentalists must in principle wait a very long time to be sure that a quasi-equilibrium state is reached. Therefore an *a posteriori* check of the validity of an experimental run and of a data report is the slowness of the temperature sweep in the vicinity of a critical point. When this is the case, many experimental points can then be measured on a narrow temperature range, and a temperature derivative can be taken with some precision and reliable physical information obtained (Ausloos and Durczewski 1980).

Such a temperature derivative is, indeed, sometimes necessary. Properties like the electrical resistivity, the thermoelectric power, the Hall resistance, etc usually behave smoothly near a phase transition, with the notable exception of the superconductivity transition. The difference arises from the type of order parameter governing the transition. A singularity in the transport coefficient is usually found if the latter describes the transport of the order parameter itself. When the transport coefficient involves the vanishing of the order parameter only in an indirect way, the coefficient behaves smoothly but its derivative can present an anomalous peak, similar to the lambda peak seen on static properties.

One might also remember that it is believed that the critical exponent of the electrical resistivity temperature derivative is the same as that of the specific heat (Fisher and Langer 1968, Balberg and Helman 1978). Therefore it is of interest to obtain an excellent fit of the data and conclusive value for the parameters. The system which remains the most illustrative and the paradigm of these remaks is Dy where different types of singularities have been found (see Ausloos and Durczewski (1980) for a critical review).

Among the latest attempts to obtain a large number of $d\rho/dT$ data points with great precision, in the truly critical region, is the study of the ferromagnetic-paramagnetic transition of the intermetallic compound TbZn (Sousa *et al* 1980). Some data analysis has been already reported in this case. It was found that the critical exponent could not be obtained without any ambiguity. A positive or negative value of the critical exponent together with a logarithmic divergence of $d\rho/dT$ could be obtained.

To reanalyse the TbZn data rather than those on Dy seems of greater value because of the higher precision obtained on one hand, and also because the transition seems more simple. In Dy, the transition is between an antiferromagnetic phase and a paramagnetic one. Therefore it is not clear whether one (or two) singular term(s) must be used in the analysis (Ausloos 1977). Furthermore, one has argued that the order parameter might change from a $n = 4$ spin model to a dipolar Ising type near the Neel temperature (Lederman 1975). In the case of TbZn, the magnetic transition is complicated by a tetragonal distortion of the unit cell *below* the Curie temperature T_c. However *above* T_c a very reliable data analysis can be made.

Many data statistical treatments exist (Green and Margerison 1977). In this paper, we will use a method proposed by Sobotta (1985). It is based on a bivariate analysis of the data (Eadie *et al* 1971). This is the first method, to our knowledge, to take into account errors on the resistivity and temperature measurements on the same footing in the critical region where the fit function is singular. It has been tested on artificial data in Sobotta's original paper. It is of interest to examine the advantages of the new method in a real case. A method (Barker and Diana 1974) giving a polynomial fit to a set of data when both variables have uncertainties does not apply here because we have to allow for a possible singularity at T_c (Laurent and Ausloos 1989).

In § 2, we recall the usual procedure to extract critical exponents from data through a log-log fit. In the case of data transformation (such as numerically taking a derivative)

before analysis, some information can be lost. More drastically, if the derivative is taken with respect to the x-axis variable, and since the latter is not obtained error free, a simple linear regression analysis is *wrong*. The fit parameters must be obtained taking into account different weights (also called 'metrics') along the x and y directions. Furthermore, the weights along the y direction depend on those along the x direction, at various data points, due to the data manipulation. (Moreover these weights can vary from point to point.) Therefore the standard 'error bars' are not strictly parallel to the x and y axes, but can be asymmetrical and be at an angle with respect to each other. Hence, a good method of fitting will necessarily have to use (bivariate) 'anisotropic metrics', as presented below.

In § 3, an application to a power-law fit of $d\rho/dT$ data on TbZn is presented, taking into acccount inherent simplification (constant weights) due to currently available data. The stability of the results with respect to Gaussian noise is also checked. A second 'numerical control' investigation is also presented by allowing for two different weights (in *a priori* chosen intervals) along the x and y axes. In this case, a log theoretical law is used as an example (to reduce computer time). Finally a combination of both tests is made. To our knowledge this sort of investigation has never been reported.

In § 4, a discussion of the results is given. It is indicated that the latter tests can imply interesting deductions on reported experimental data or runs. A comparison with the best estimates corresponding to this work is made. Some caution is given about definite conclusions in related similar works (§ 5).

2. Bivariate least-squares method

The usual procedures to determine critical exponents and critical amplitudes start from the power-law expression

$$(1/\rho_c)(d\rho/dT) = C + D\varepsilon^{-\lambda} \tag{1}$$

or, when the exponent is equal to zero, from a logarithmic expression

$$(1/\rho_c)(d\rho/dT) = A\ln(T - T_c) + B \tag{2}$$

where the expressions are written for the electrical resistivity data near the critical temperatures T_c, with $\varepsilon = (T - T_c)/T_c$ and $\rho_c = \rho(T_c)$. The unknowns are the amplitudes A, B, C and D, and the critical exponent λ. The critical temperature T_c is often fixed during data fitting. Afterwards, one lets T_c sweep through the critical region, and searches for the minimum error bars on the parameters (Sousa *et al* 1980).

A well known point of controversy stems from the fact that $d\rho/dT$ is not measured directly, but is obtained from a numerical derivative ($d\rho/dT = \Delta\rho/\Delta T$) of the data on the electrical resistivity ρ. This implies dividing two small numbers to obtain some 'reasonable' value. Furthermore, authors may obtain such a derivative either directly from neighbouring points or after data smoothening through, e.g., some spline or polynomial function. Other authors take the derivative from the rough data and smooth the resulting data later. Sometimes a 'background' is subtracted so that B or $C = 0$. The critical exponent λ is then obtained, simply speaking, from a least-squares analysis of a log–log plot.

The major problem obviously arises from the inherent errors in measuring (in fact , a voltage drop across the sample) the temperature T, and their propagation in the data transformation. In the case of smooth functions the total mean error for

independent errors on ρ and T may be approximately calculated through the Gauss linear superposition formula (Dacunha-Castelle and Duflo 1982). However for power-law or logarithmic-law expressions like (1) and (2), the probability distributions of the errors on $\ln|T-T_c|$ and $\ln|d\rho/dT|$ cannot be assumed to be directly obtained from those on T and ρ. Often, one further assumes that T measurements are error free, or that error bars on T are constant. However, this leads to another difficulty inherent in the experimental conditions when taking data near a critical point. For better precision, quasistatic conditions must be maintained. Hence very small temperature steps must be monitored. It thus happens that the temperature difference $(T_c - T)$ is of the same order of magnitude as the mean error D_T on T, in particular near T_c, where the best precision is looked for. As pointed out by Sobotta (1985), this may lead to the interpretation of the data in terms of a crossover between exponents near T_c, i.e. a crossover between different models (see above).

Therefore one has to avoid parametric fits influenced by data manipulation and to use a method which tests 'composite hypotheses'! The bivariate method requires the minimisation of the sum V_N of the local maximum likelihood estimators V_i (Eadie *et al* 1971)

$$V_N = \sum_{i=1}^{N} V_i = \sum_{i=1}^{N} \frac{(T_i - \bar{T}_i)^2}{D^2(T_i)} + \frac{(\rho_i' - \bar{\rho}_i')^2}{D^2(\rho_i')} \tag{3}$$

for the N data points $\rho'(T_i)$ in terms of the critical amplitudes in $\rho' \equiv d\rho/dT$, but also for the unknown temperatures T_i defined by $\bar{\rho}_i' = \rho'(\bar{T}_i)$ and where the fitting curve is thus $\bar{\rho}'(\bar{T})$. One has thus to minimise a function of $N + N_A$ parameters where N_A is the number of critical parameters: $N_A = 4$ and $N_A = 3$ in (1) and (2), respectively. In the following, we will instead use the normalised maximum likelihood estimator

$$V = V_N/N. \tag{4}$$

The errors on ρ' and T are assumed to be distributed according to (here arbitrary but known distributions) $D(\rho')$ and $D(T)$, respectively. The method therefore consists of obtaining the smallest distance between the data points (ρ_i', T_i) and the theoretical law $(\bar{\rho}_i', \bar{T}_i)$ in an anisotropic metric defined by $D(\rho')$ and $D(T)$ (Lybanon 1984, Mantri 1984).

In order to speed up the minimisation procedure, and avoid searching for minima in an $N + N_A$ parameter space, one first minimises V_i with respect to T_i and then minimises V_N with respect to the N_A remaining parameters.

The method outlined so far is very general, but it is now applied to a more simple case where

$$D(T_i) = D_T \qquad \text{and} \qquad D(\rho_i') = D_{\rho'} \tag{5}$$

since other authors consider the error bars to be constant. Therefore, we will use such an approximation in the next section, but will test it afterwards.

3. The case of $\rho'(T)$ in TbZn near T_c

3.1. Data as taken

In our opinion, the most precise data on a transport property to analyse in the vicinity of a critical point are those of Sousa *et al* (1980) on the temperature derivative of the

electrical resistivity on TbZn. Furthermore they have been analysed along classical lines (assuming $D(T)=0$) and are easily available (Amado 1984). They are shown in figure 1(*a*). According to Amado (1984) the error on the temperature measurement is constant and approximately equal to $D_T=0.0003$ while that on $\mathrm{d}\rho/\mathrm{d}T=\rho'$ is equal to $D_{\rho'}=0.01$. The $N=36$ data points examined are those in the critical region, which has been determined after fitting the overall ρ' curve to a $(T-T_c)^{-1/2}$ law in order to eliminate the classical ('fluctuation free') region. The 'first' estimate of T_c is 199.54 K. Hence the critical region extends from about $\varepsilon=7\times10^{-3}$ to $\varepsilon=7\times10^{-4}$. According to previous analysis (table 1 in Sousa *et al* 1980) an accurate guess of the parameters in (2) is

$$T_c=199.54\ \mathrm{K} \qquad A_0=-0.3\times10^{-2} \qquad B_0=0.3\times10^{-2}. \tag{6}$$

These three values are used as the starting point of the minimisation routine. The best fit to (2) is found for (see table 1)

$$T_c=199.533\ \mathrm{K} \qquad A=-0.141\ 13\times10^{-2} \qquad B=0.313\ 35\times10^{-2} \tag{7}$$

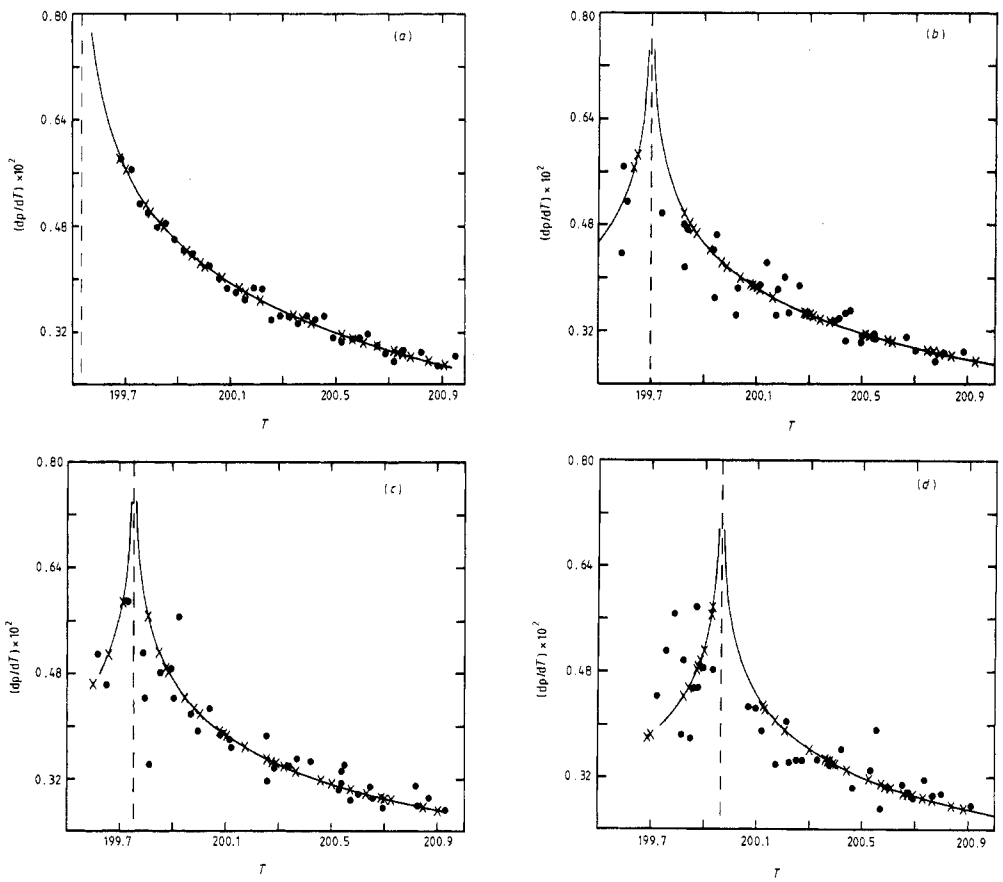

Figure 1. Temperature derivative of the electrical resistivity of TbZn. Data of Sousa *et al* (1980) (circles). (*a*) Fit to (2) assuming a logarithmic singularity (crosses) assuming $D_T=0.0007$ and $D_{\rho'}=0.01$ (see text for notation). (*b*)-(*d*) Fit to Gaussian modified data with a probability distribution given by (9). Initial conditions and numerical values of the parameters are found in table 3.

Table 1. Data analysis of the electrical resistivity temperature derivative of TbZn near the critical temperature T_c assuming a logarithmic singularity. Notation as in text. The first line of each run corresponds to the 'initial values', the second line to the best resulting fit.

$(1/\rho_c)(d\rho/dT) = A \ln\lvert T - T_c\rvert + B$						
D_T	$D_{\rho'}$	N	A	B	T_c	V
7 (−4)	1 (−2)	36	3 (−3)	3 (−3)	199.54	
			−1.4 (−3)	3.1 (−3)	199.53	0.199
		36	3 (−3)	3 (−3)	199.64	
			−1.4 (−3)	3.1 (−3)	199.53	0.199
		33	3 (−3)	3 (−3)	199.54	
			−1.6 (−3)	3.2 (−3)	199.47	0.142
		33	3 (−3)	3 (−3)	199.64	
			−1.6 (−3)	3.2 (−3)	199.47	0.142
		31	3 (−3)	3 (−3)	199.54	
			−1.5 (−3)	3.1 (−3)	199.50	0.131
		31	3 (−3)	3 (−3)	199.64	
			−1.5 (−3)	3.1 (−3)	199.50	0.131
7 (−5)	2 (−2)	36	−3 (−3)	3 (−3)	199.54	
			−1.26 (−3)	3.07 (−3)	199.57	1.80
5 (−5)	1 (−2)	36	−3 (−3)	3 (−3)	199.54	
			−1.31 (−3)	3.09 (−3)	199.56	1.99

which corresponds to $V = 0.1977$ (figure 1(a)). Since the precision of the original data is a rather rough estimate, another trial fit has been made assuming $D_T = 0.000\,05$ but keeping $D_{\rho'} = 0.01$ and the initial values (6). It has been found that the best fit occurred for

$$T_c = 199.563 \qquad A = -0.131\,27 \times 10^{-2} \qquad B = 0.309\,88 \times 10^{-2} \tag{8}$$

which leads to a larger $V = 1.993\,15$ (figure 2(a)). For a narrower error margin on the temperature the minimised maximum likelihood increases. Thus the *a priori* estimated mean error imposes a drastic constraint effect on the fit. Other cases are also given in table 1 and correspond to different initial conditions.

The power-law theoretical prediction (1) has also been tested under various initial conditions (table 2). The case $D_{\rho'} = 0.02$ and $D_T = 7 \times 10^{-5}$ is graphically displayed in figure 3. In this case, a negative initial value of λ was assumed. The initial values of C and D have been taken as a rough guess based on an order of magnitude argument. The number of data points was arbitrarily reduced to $N = 33$. We eliminated the three data points furthest away from T_c in order to emphasise the importance of the critical region, i.e. the value of the 'Ginzburg-reduced temperature' was reduced ($\varepsilon_G = 5 \times 10^{-3}$) in order to avoid effects (if any) of the 'classical' regime. Other cases also are given in table 2 for different initial conditions.

3.2. Gaussian-modified data

Measurements are subject to various errors: besides the sensitivity of the data acquisition instruments, systematic errors can also be unwittingly introduced by the experimentalists. The size of error bars is sometimes quite debatable. (It is known that the

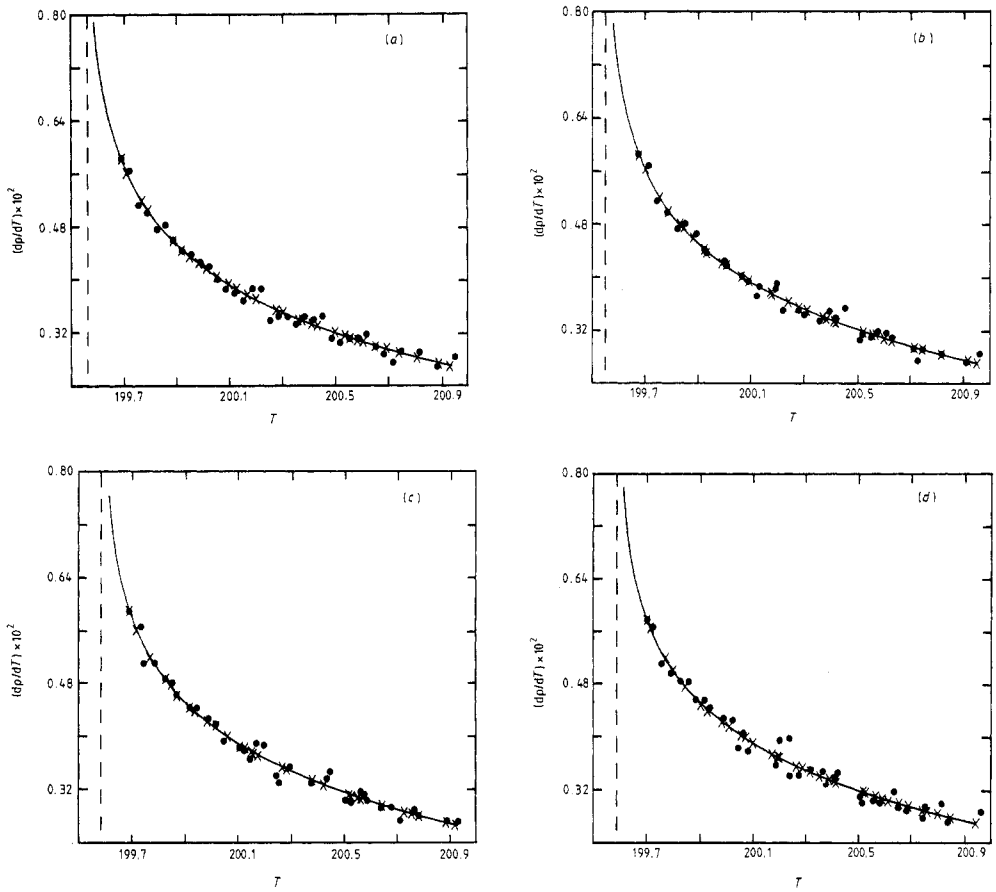

Figure 2. Temperature derivative of the electrical resistivity of TbZn. Data of Sousa *et al* (1980) (circles). (*a*) Fit to logarithmic singularity (equation (2)) (crosses) with $D_T = 0.000\,05$ and $D_{\rho'} = 0.01$ (see text for notation). (*b*)-(*d*) Fit of logarithmic law (2) to Gaussian-modified data. Initial conditions and numerical values of the parameters are found in table 3.

Table 2. Data analysis of the electrical resistivity temperature derivative of TbZn near the critical temperature T_c assuming a power-law behaviour. Notation as in text. The first line of each run corresponds to the 'initial values', the second line to the best resulting fit.

$$(1/\rho_c)(\mathrm{d}\rho/\mathrm{d}T) = C + D(|T - T_c|/T_c)^{-\lambda}$$

D_T	$D_{\rho'}$	N	C	D	T_c	λ	V
7 ((−3)	1 (−2)	33	1 (−2)	−1.05 (−2)	199.54	−0.3 (−1)	
			1.8 (−2)	2.6 (−2)	199.52	−0.98 (−1)	0.14
		33	1 (−2)	−1.05 (−2)	199.58	−0.3 (−1)	
			8.3 (−3)	−2.2 (−2)	199.62	−0.27 (0)	0.138
		33	1 (−2)	−1.05 (−2)	199.64	−0.3 (−1)	
			6.2 (−3)	−3.2 (−3)	199.69	−0.42 (0)	0.137
7 (−5)	2 (−2)	33	1.0 (−2)	−1.05 (2)	199.64	−0.3 (−1)	
			9.62 (−3)	−1.91 (−2)	199.63	−0.2 (0)	1.7

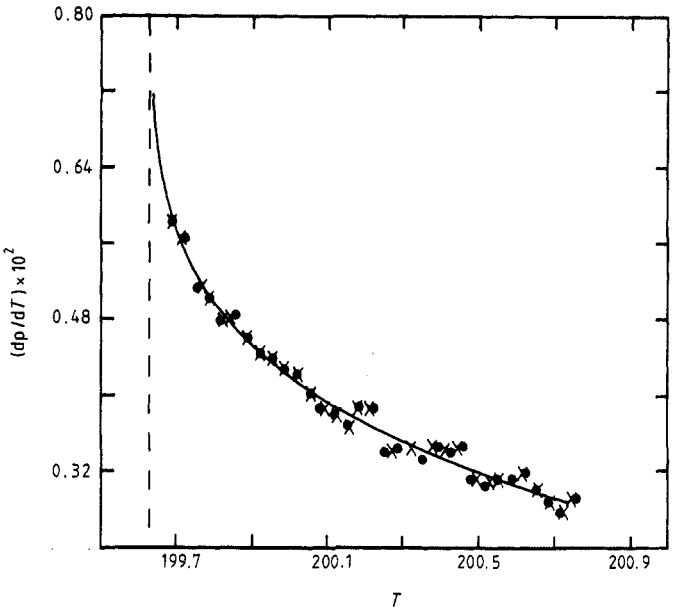

Figure 3. Temperature derivative of the electrical resistivity of TbZn (Sousa *et al* 1980) (circles). Fit to power-law expression (1) (crosses) with a negative critical exponent.

'best modern values' of fundamental *constants* fall outside error bars of not so old measurements; see Dufour (1987).)

On the other hand, it is interesting to observe the stability of the above results. Initial conditions have some influence on the convergence and the final values but have reasonably understandable effects. Data rounding errors are less obvious. Therefore we have slightly modified the data as taken. Furthermore, by allowing for a small Gaussian deviation from the data points, and by randomly generating such an error, we (hopefully) reproduce a set of experimental runs which would take a long time to perform in the laboratory.

The probability distribution of Gaussian errors on T and ρ' is given by the Gauss expression (Dacunha-Castelle and Duflo 1982)

$$D(T_i, \rho_i') = \frac{1}{2\pi} D_T^{-1} D_{\rho'}^{-1} \exp\left(-\frac{(T_i - \bar{T}_i)^2}{2D_T^2} - \frac{(\rho_i' - \bar{\rho}_i')^2}{2D_{\rho'}^2} \right). \tag{9}$$

Results for different runs, i.e. with different values of D_T and $D_{\rho'}$, are given in table 3. The first line of each run corresponds to the data as taken. In figure 1(b)-(d) we show the results concerning a particular run together with the fit to the data as taken (figure 3(a)) for the assumed value of D_T and $D_{\rho'}$ (table 3).

In order to show the drastic influence of weak fluctuations in the generated data randomness, we show in figure 2 (b)-(d) results for another run, assuming the same error on ρ' but with smaller precision on the T measurements. Numerical values are found in table 3.

3.3. *Variable weight test*

A second 'numerical control' investigation on the apparent variability of results can test the assumption that D_T and $D_{\rho'}$ are constant during the experimental runs (e.g.

Table 3. Same as table 1, but allowing for an extra arbitrary distribution of errors on each data point. The first line corresponds to the initial values. The next lines correspond to the investigated 'Gaussian randomly modified' data.

$(1/\rho_c)d\rho/dT = A\ln(\lvert T - T_c\rvert) + B$							
D_T	$D_{\rho'}$	N	A	B	T_c	V	Figure
Initial conditions			−3 (−3)	3 (−3)	199.54	—	
5 (−5)	1 (−2)	36	−1.31 (−3)	3.098 (−3)	199.563	1.99	2(*a*)
			−1.318 (−3)	3.131 (−3)	199.548	2.05	2(*b*)
			−1.282 (−3)	3.03 (−3)	199.584	2.32	2(*c*)
			−1.247 (−3)	3.06 (−3)	199.589	3.84	2(*d*)
7 (−5)	2 (−2)	36	−1.31 (−3)	3.09 (−3)	199.563	0.572	
			−1.30 (−3)	3.4 (−3)	199.596	0.794	
			−1.27 (−3)	2.99 (−3)	199.595	1.20	
			−1.23 (−3)	3.05 (−3)	199.594	1.93	
7 (−4)	3 (−2)	36	−1.31 (−3)	3.09 (−3)	199.563	0.28	
			−1.27 (−3)	3.14 (−3)	199.553	0.555	
			−1.30 (−3)	2.95 (−3)	199.547	1.01	
3 (−5)	3 (−2)	36	−1.31 (−3)	3.10 (−3)	199.562	0.303	
			−1.24 (−3)	3.12 (−3)	199.571	0.584	
			−1.34 (−5)	2.97 (−3)	199.583	1.050	
7 (−4)	1 (−2)	36	−1.411 (−3)	3.13 (−3)	199.533	0.198	1(*a*)
			−0.978 (−3)	2.95 (−3)	199.699	0.738	1(*b*)
			−0.966 (−3)	2.83 (−3)	199.752	0.925	1(*c*)
			−0.908 (−3)	2.63 (−3)	199.964	0.887	1(*d*)

because quasistatic conditions are maintained). In order to have a simple test on this assumption, the errors (D_T and $D_{\rho'}$) have been *arbitrarily* doubled after and including the 13th data point away from the initial input value of T_c. Resulting fits are not shown, but it is clear that the fit has to become *more precise* since larger 'error bars' are allowed: the crosses 'fall' much more on the theoretical curve. In this test, it has been assumed that the singularity is logarithmic. This reduces the number of parameters to be calculated. This law is also 'more physically' accepted in general (Ma 1976).

The resulting parameter values for A, B, T_c and V are given in figures 4-6 as a function of the number i of data points. It is also readily seen that the convergence is much smoother in this 'double weight' case. This shows the necessity of accurately defining standard error bars on data points, and the need to consider them in statistical analysis. This can also be an *a posteriori* check on the data. In particular, one can state that the precision of the data was likely to be varying in Sousa *et al* (1980), even though strict quasi-equilibrium conditions were maintained and the numerical derivative technique used was optimised to keep as much information in the data as possible.

3.4. Gaussian-modified data and variable weights

Fifty Monte Carlo simulations of (2), taking values of $D_T = 5\times10^{-5}$ and $D_{\rho'} = 10^{-2}$ with error doubling starting at (and including) the 13th data point away from the initial value $T_c = 199.54$ K have finally been made. The initial values and the results are given in table 4 together with the correlation coefficients (Dacunha-Castelle and

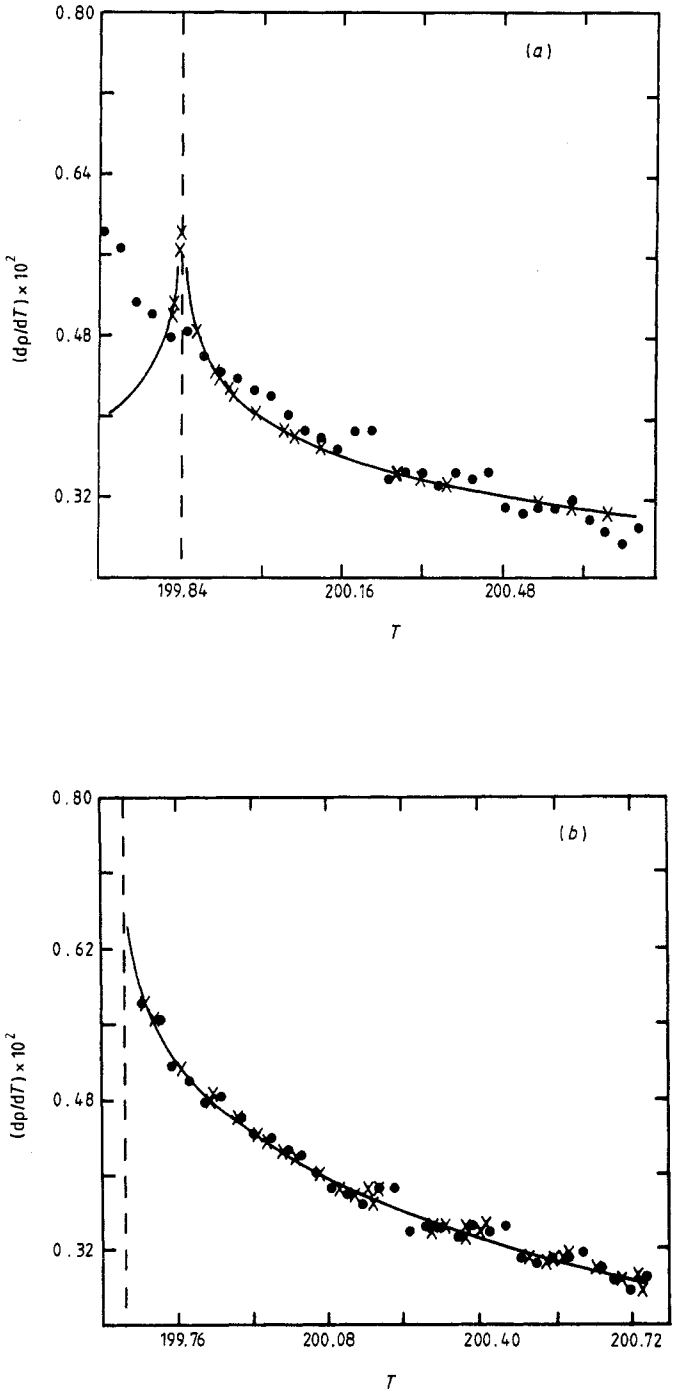

Figure 4. Temperature derivative of the electrical resistivity of TbZn data (circles) from Sousa *et al* (1980). (*a*) and (*b*) crosses: fit to (10). Initial values and resulting parameter values are given in table 5.

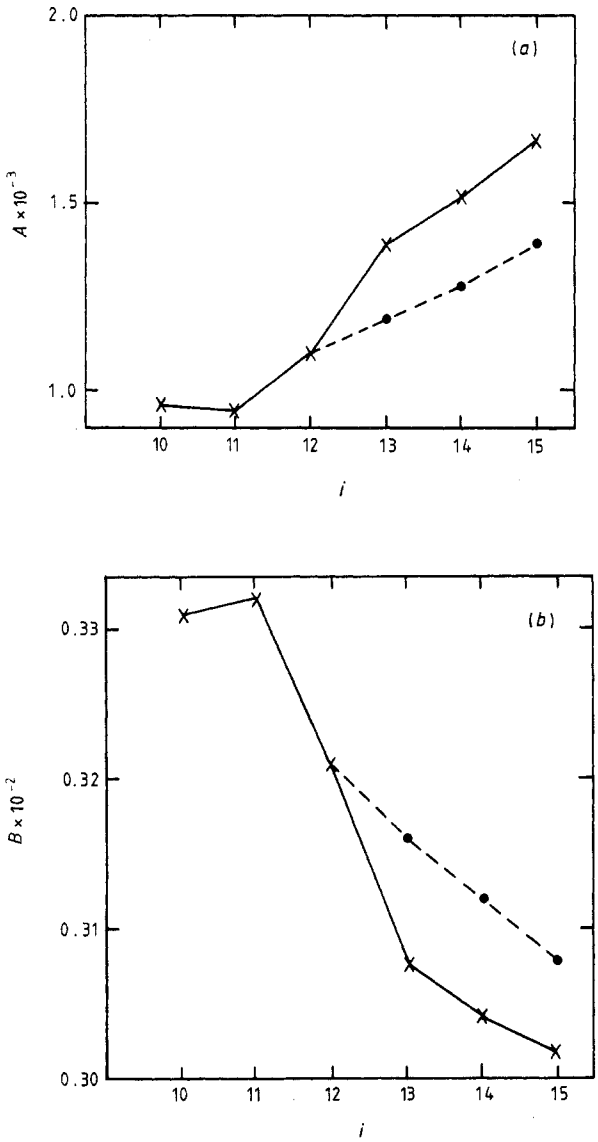

Figure 5. Critical amplitudes A and B of the logarithmic singularity in the electrical resistivity temperature derivative of TbZn as a function of the number of data points under the assumption of constant uncertainty in the data (full curve) and allowing for a constant but twice as great uncertainty starting from and including the 13th data point away from the critical temperature (broken curve).

Duflo 1982)

$$r(x, y) = \frac{1}{L} \sum_{n=1}^{L} (x_n - \bar{x})(y_n - \bar{y}) D^{-1}(x) D^{-1}(y)$$

for the variables x and y, and where $D(x)$ (or $D(y)$) are the mean square root of the variance (the 'standard deviation'). The values obtained by Sousa *et al* (1980) are also given. The parameters B and T_c are almost identical to ours though the amplitude A

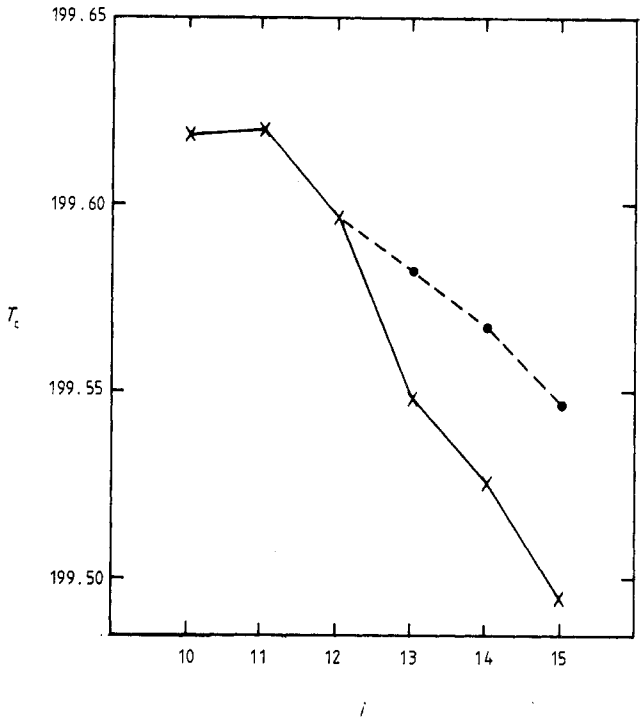

Figure 6. Critical temperature of TbZn as determined by fitting the electrical resistivity temperature derivative to a logarithmic law near T_c assuming constant uncertainty in the data (full line) and allowing for constant but twice as great uncertainty at and after the 13th data point away from T_c (broken line).

Table 4. Critical amplitudes and critical temperature of a 50 run Monte Carlo simulation of the TbZn electrical resistivity temperature derivative data (Sousa *et al* 1980) near the critical temperature, for 36 data points above the critical temperature. Correlation coefficients between amplitudes and with respect to the critical temperature are also given.

$(1/\rho_c)(d\rho/dT) = A \ln|T - T_c| + B \qquad N = 36$

	D_T	D_ρ	A	B	T_c
Initial values	5 (−5)	1 (−2)	−3 (−3)	3 (−3)	199.540
Output values ($L = 50$ runs)			−1.303 (−3)	3.096 (−3)	199.565
Standard deviation			±6.454 (−5)	±3.116 (−5)	±0.023
Sousa *et al* (1980)			−3.02 (−3)	3.10 (−3)	199.56

Correlation coefficients

(A, B)	(A, T_c)	(B, T_c)
−0.7662	0.9571	−0.8893

is rather different. Correlation coefficients with respect to T_c have an absolute value around 0.9 which is acceptable though the correlation between A and B is rather weak.

4. Discussion of results

The first conclusion reached, from perusal of table 1, concerns the great stability of the results against initial conditions. The critical temperature and the critical amplitudes are rather well determined. The critical exponent λ is, however, less accurately determined. The number of data points taken has a small but unclear influence. For example, the critical temperature shift does not seem directly proportional to the number of data points taken.

Another remarkable fact is due to the assumed error D_T and $D_{\rho'}$. The maximum likelihood estimator becomes larger when D_T or $D_{\rho'}$ decreases as expected from (3). However such a quantity appreciably varies from data run to data run when a Gaussian error is arbitrarily introduced in the data (table 3). The order of magnitude of V_N varies in a non-systematic way.

In order to understand the causes of such observations two other numerical investigations have been made. First the power-law theoretical formula (1) has been modified to

$$(1/\rho_c)(\mathrm{d}\rho/\mathrm{d}T) = \frac{A}{\alpha}\left(1 - \left|\frac{T - T_c}{T_c}\right|^{-\alpha}\right) + B_2. \tag{10}$$

A direct correspondence to (1) exists between the coefficients and the exponent. One has

$$\lambda \leftrightarrow \alpha \tag{11a}$$

$$D \leftrightarrow -A/\alpha \tag{11b}$$

$$C \leftrightarrow B_2 + A/\alpha. \tag{11c}$$

In the limit $\alpha \to 0$, (10) leads to

$$(1/\rho_c)(\mathrm{d}\rho/\mathrm{d}T) = A \ln \varepsilon + B_2 \tag{12}$$

which is (2), and where the constants are α independent. The only difference with (2) is in the amplitude of the temperature-independent term

$$-A \ln T_c + \mathrm{B}_2 \leftrightarrow \mathrm{B}. \tag{13}$$

It was observed by Amado (1984) and Amado *et al* (1988) that equation (1) leads to (Sousa *et al* 1980)

$$\mathrm{d}\rho/\mathrm{d}T = 10.040 - 10.460\varepsilon^{0.013} \tag{14a}$$

with

$$T_c = 199.56\ \mathrm{K} \tag{14b}$$

while (10) leads to

$$\mathrm{d}\rho/\mathrm{d}T = 10.565 - 10.922\varepsilon^{0.011} \tag{15a}$$

with

$$T_c = 199.56\ \mathrm{K}. \tag{15b}$$

Table 5. Data analysis of the electrical resistivity temperature derivative of TbZn near the critical temperature T_c assuming a power-law behaviour where amplitudes are independent of the critical exponent α when the latter goes to zero.

$(1/\rho_c)(d\rho/dT) = (A/\alpha)(1-\varepsilon^{-\alpha}) + B_2 \qquad \varepsilon = |T - T_c|/T_c$

D_T	$D_{\rho'}$	N	A	B_2	T_c	α	V	Figure
7 (−4)	1 (−2)	36	−9.5 (−4)	−2.6 (−4)	199.64	−0.13	—	
		36	−8 (−4)	−7.0 (−4)	199.81	−0.06	1.11	
		33	−9.5 (−4)	−2.6 (−4)	199.54	−0.13	—	
		33	−8.0 (−4)	−7.2 (−4)	199.85	−0.059	0.95	
		33	−9.5 (−4)	−2.6 (−4)	199.51	−0.13	—	
		33	−2.5 (−3)	−7.6 (−3)	199.51	−0.092	0.14	
		33	−9.5 (−4)	−2.6 (−4)	199.64	−0.13	—	4(*a*)
		33	−8.07 (−4)	−7.12 (−4)	199.84	−0.06	0.96	4(*a*)
		31	−9.5 (−4)	−2.6 (−4)	199.64	−0.13	—	
		31	−8.1 (−4)	−7.1 (−4)	199.87	−0.059	0.68	
7 (−5)	1 (−2)	33	−9.5 (−4)	−2.6 (−4)	199.51	−0.093	—	4(*b*)
			−5.4 (−2)	−1.2 (−2)	199.64	−0.264	4.9	4(*b*)
7 (−4)	2 (−2)	33	−9.5 (−4)	−2.6 (−4)	199.54	−0.013	—	
			−3.8 (−3)	−9.5 (−3)	199.62	−0.20	1.7	

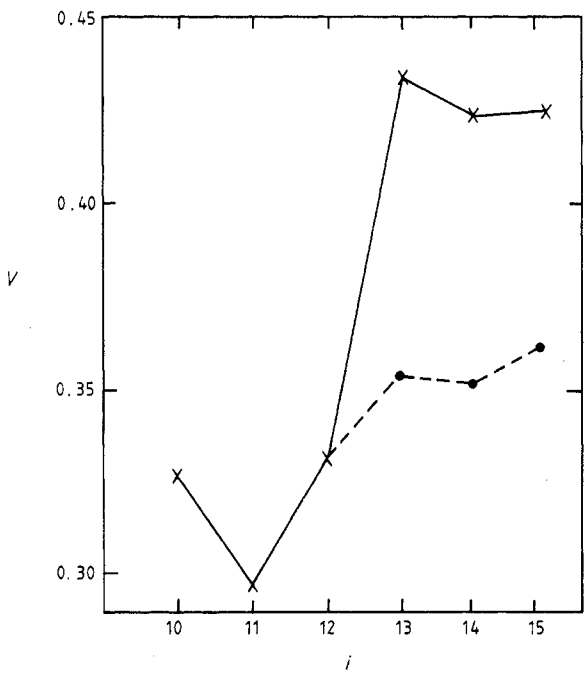

Figure 7. Maximum likelihood estimator as a function of the number of data points for the fit of the electrical resistivity temperature derivative of TbZn near the critical temperature when a constant uncertainty is assumed for all data points (full curve) and when the uncertainty is arbitrarily doubled at the 13th data point (broken curve).

The above results considered no uncertainty on T (or on ρ'). We thus used our method to examine the behaviour of (10). Results are reported in table 5. One concludes that the *critical exponent appears systematically smaller* than in table 2, except for the best case of table 2 and table 5, where it is equal and where the maximum likelihood estimator is the same. Taking (11) into account, the amplitudes are nevertheless different.

A classic test is the examination of the stability of T_c. From table 5 one can see that T_c may vary between 199.87 and 199.51, which seems a rather large variation when good experimentalists usually report a precision of the order of 10^{-5} on measuring the temperature.

Notice also the very important information resulting from our fitting procedure: a 'very precise' measurement of T or ρ' does not imply that the best data point (as determined from the local maximum likelihood estimator) falls on the theoretical curve (e.g. figure 4(b)). The anisotropic metric only finds the shortest distance to the theoretical curve.

Furthermore, the procedure allows for finding that T_c has not been appropriately guessed, but could be quite different (figure 1(b)-(d)). In this case, one could relax the assumption of the same amplitudes and exponents on each side of T_c. This has not been done here to keep numerical work at a reasonable value, i.e. less time consuming, for this report. Extensions would be useful.

5. Conclusion

From this analysis one can conclude that much work remains to be done if one wants to obtain and understand critical amplitudes and critical exponents and, consequently, theoretical laws for the behaviour of singular physical properties in the vicinity of a phase transition. The asymptotic behaviour of singular curves is very difficult to handle. This bivariate method brings much to the data analysis, since it takes account of experimental uncertainties in the measured variables, and may take into account numerical data treatment prior to the 'critical data analysis'. It can allow for regularity and irregularity at a critical point, but does not bring a final point to data analysis as of now.

One can understand from the above that almost 'any value' can be obtained. Many authors have attempted to convince readers (and themselves) about critical point values resulting from a particular analysis, sometimes forcing expected values to emerge from an analysis by throwing away 'strange' data points. The above method, which takes into account error bars (which may be large) on data points, avoids such a data handling procedure. Moreover it is seen that defining a small error on say, temperature is *essential* in obtaining not only a reasonable value of the critical temperature and of the critical amplitudes, but certainly also for the critical exponent. Hence greater confidence can be expected in the future if the above rules are respected in reporting data.

One valuable input of the theory is the possibility of using an anisotropic metric for measuring the distance between the theoretical curve and the data point. This is also very useful for other types of analysed functions: discontinuous, multisingular or piecewise-defined functions. It has to be modified to analyse critical point singularities from power series expansions (Arteca *et al* 1985) but could be used to check convergence radius.

In the particular case which is examined here, it is *a posteriori* observed that the method is extremely sensitive to the handling of experimental uncertainties and to inform on hidden lack of data precision. The observation of a possible variation in D_T and D_ρ, in the vicinity of T_c does not imply bad data acquisition nor the lack of a quasi-equilibrium condition, but rather shows the need for more precise information before the efficient data analysis. Plotting test output data as in figure 7 is *very meaningful*, but is done very rarely.

Finally, the method used here combined with data simulation seems to be of interest. The time spent in 'better data definition' by experimentalists in a laboratory might be regained in the data analysis when computer experiments can be performed as here, i.e. supplementing data with Monte-Carlo-like physics.

This work has again shown the uncertainty in attributing values to critical amplitudes and the difficulty of having a definite conclusion on the sign or value of the critical exponents resulting from experimental work. Although the critical exponent is found to be positive here for $d\rho/dT$ in TbZn, it does not mean that it would remain positive if the amplitude were allowed to differ on both sides of T_c. This is another problem to be investigated. Last, but not least, the need to obtain more information on error bars about such experimental data if elaborate data analysis is undertaken has been pointed out.

Acknowledgments

Many thanks are extended to Professor J B Sousa and Dr M M Amado for enlightening discussions on experimental conditions and for making available and allowing me to quote data from Dr Amado's PhD thesis. Thanks also to Dr G Sobotta for explaining the basis of the theoretical method, and to Mrs V Brück for her patience and assistance in running the program on the CYBER 175 at the University of Bochum. A Nato grant and the CGRI Commissariat General aux Relations Internationales Bruxelles financial support are acknowledged and have made possible exchanges between Porto and Liège.

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