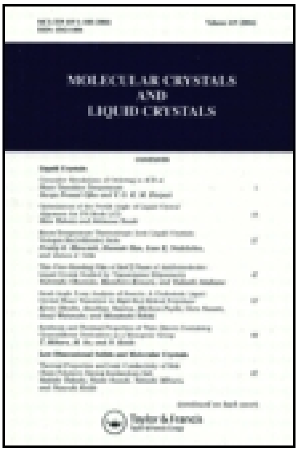

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Global Order Parameter Critical Exponent: A Different Calculation Approach

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Global Order Parameter Critical Exponent: A Different Calculation Approach

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In this paper we present an approach that permits to study the behavior of the nematic phase's order parameter exponent (β) for all temperatures of the phase; our method makes an independent calculation of β for each temperature value T. *Here use hypothetical data to analyze the consistence of the results, the limitation of the experimental data usability and the influences of the experimental errors on the β(*T*) curves. After that, we use experimental data to show that the order parameter critical-like exponent presents a constant behavior along the entire domain of the nematic phase.*

Keywords Nematic phase; order parameter; critical exponent

1. Introduction

The nematic phase is the simplest liquid crystalline phase but, despite this simplicity, its theoretical and phenomenological descriptions are far from being complete. Among the most challenging problems we have the studies on the critical-like behavior of the nematic-isotropic (NI) phase-transition [1,2]. The nature of NI phase-transition itself has been a question of considerable controversy. Namely, it is well known that it is a first order phase-transition [3,4], but due to its small latent heat [4], it is accompanied by the same kind of large fluctuations that characterize the neighborhood of the critical point of a continuous phase-transition [1,2]. The experimental determination of the equivalence class of these fluctuations is a difficult task. For example, the results obtained by Keyes and Shane [5], in 1979, pointed that the NI phase-transition presents tricritical-like exponents. Four years after, Rosenblatt [6] showed that the classical mean-field exponents are also compatible, opening an endless controversy on the determination of the critical-like exponents of this transition. Until the temperature extension of NI phase-transition critical-like region has been under constant discussion [1,2].

The first work pointing the existence of some kind of the critical exponent to the nematic phase's order parameter S was carried out by Haller in 1975 [7]. In his paper Haller showed that S can be fitted by a single power law function and, by means of a least squares fit on the birefringence data of several nematic liquid crystals (NLCs), he observed a near universality of the order parameter exponent: $\beta = 0.17$–0.23 [7]. He introduced the question of what is the theoretical significance of this universality, but himself admitted the poor theoretical significance of his approximation to the thermal behavior of S. In 2000, Marinelli and Mercuri [8] studied β using the anisotropy in the thermal conductivity of

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the *m*CB (4-n-*m* alky-4-cyanobiphenyl, $m = 5$–8) homologous series. Now, using a fit equation compatible with the weakly first-order character of NI [9] phase-transition, their results showed the consistence between the measurements and the tricritical value $\beta = 0.25$. Same conclusion was obtained by Chirtoc et al. [9] in 2004. More recently, 2012, Lenart et al. [10] obtained the value $\beta = 0.28 \pm 0.03$ using E7's nonlinear optical birefringence data.

Despite the concordance between results obtained by different authors, there are many unclear points in their analyses. A first problem comes from the determination of the critical region itself; may we use data out of this region to measure the critical-like exponent. A second problem is: there are some apparent ambiguities on the determination of the values by means of least squares fit algorithms. Using a four free parameter fit equation, Marinelli and Mercuri [8] and Chirtoc et al. [9] obtained, in some cases, values not consistent with the tricritical model. To assure the compatibility of the results, they fitted again the data using a fixed $\beta = 0.25$, showing that the new fit parameters are also statiscally relevant.

In the present work, we present a different approach to calculate the exponent of S [11]. The main motivation is to overcome the problems pointed above. The paper is organized as follows. In the next section, we will show our approach, we will analyze the consistence of the results, the limitations of the experimental data usability and the influences of the experimental errors on the results obtained. After that, we will use the approach to analyze some experimental data found in the liquid crystals (LCs) literature.

2. The Calculation Approach

2.1 Transcendental Equation

Our starting point is the expression of the dependence of the order parameter S with the temperature T commonly used to fit the order parameter data [8,9]:

$$S(T) = S^{**} + c_0(T^{**} - T)^{\beta(T)}, \tag{1}$$

where S^{**} is the value of S at the effective second order critical temperature T^{**}, β is the critical-like exponent and c_0 is a constant. This function is compatible with the weakly first-order character of the NI phase-transition [9]. We are explicitly considering the order parameter exponent as being temperature dependent—this fact will get clear when we see the calculation method.

Haller's [7] approach takes $S^{**} = 0$, being this normalization of S at the quasi-critical temperature the cause of the inconsistence of the obtained exponent and the theories of the NI phase-transition. The best fitting algorithms calculate all these four free parameters but, due the internal dependence between them, usually the results obtained are not conclusive. To surpass these problems, our idea is to use experimental data to diminish the number of free parameters. Let us to define:

$$S(T_1) \equiv S_1, \tag{2}$$

$$S(T_M) \equiv S_M, \tag{3}$$

being T_1 the temperature closest to the nematic-crystalline (NK) phase-transition temperature T_{NK}, or the lower temperature in the nematic phase where the data have been taken.

T_M we define as:

$$T_M \equiv T^{**} - \Delta \Leftrightarrow T^{**} = \Delta + T_M, \quad (4)$$

i.e., T_M represents a temperature that is, by an amount of Δ, less than T^{**}. Among the experimental data, this is the measured value closest to the NI phase-transition temperature T_{NI}. T_{NI} must be between the temperature interval T_M and $T_M + \Delta$.

Using these definitions, by straightforward calculation one can write one equation to S depending only on two free parameters:

$$S(T) = \frac{S_M - S_1\left(\frac{\Delta}{\Delta+T_M-T_1}\right)^{\beta(T)} + \left(S_1 - S_M\right)\left(1 - \frac{T-T_1}{\Delta+T_M-T_1}\right)^{\beta(T)}}{1 - \left(\frac{\Delta}{\Delta+T_M-T_1}\right)^{\beta(T)}}. \quad (5)$$

Finally, from this equation we construct a transcendental equation to $\beta(T)$;

$$\beta(T) = \frac{\ln\left[\frac{S_M - S(T) + [S(T) - S_1]\left(\frac{\Delta}{\Delta+T_M-T_1}\right)^{\beta(T)}}{S_M - S_1}\right]}{\ln\left(1 - \frac{T-T_1}{\Delta+T_M-T_1}\right)}. \quad (6)$$

Our procedure will solve this equation for each experimental data $S(T)$ obtaining a corresponding $\beta(T)$ value. Most important fact is that each β is independent from the others. Of course, the delimiting measurements $S(T_1)$ and $S(T_\mathrm{M})$ affect the $\beta(T)$ curve as a role. We will analyze the consequences later.

2.2 Data Usability and Limits

In our analysis we consider a given data set $S[i]$ and $T[i]$, $i = 1, 2, \ldots, M$. $S[i] \equiv S(T[i])$ is the ith value measured to S and M is the number of measured points. We arrange the data in such way that $T_1 = T[1]$ and $T_\mathrm{M} = T[M]$, with the temperature increasing with the increasing of i. In this way; $S_1 = S[1]$ and $S_M = S[M]$.

The first observation on the calculation of $\beta(T)$ from Eq.(6) is: One can use any physical property that is directly proportional to S. In fact, linear transformations on the values of S and T have no effect on the $\beta(T)$ values and, therefore, they are not influenced by global systematic errors on the measurements.

We have to look with attention for the two temperature ending points; T_1 and T_M. If the experimental data measured at these points are used in Eq.(6), we have:

$$\beta(T_1) = \frac{\ln 1}{\ln 1},$$
$$\beta(T_M) = \beta.$$

That is, the data measured at T_1 gives an undefined equation and the data measured at T_M invalidates the use of Eq.(6) as a transcendental equation. Therefore, Eq.(6) is useful to calculate $\beta(T)$ within the interval $T_1 < T < T_\mathrm{M}$ and for each data set with M points we have a $\beta(T)$ curve with $M - 2$ values.

2.3 Algorithm Construction

Using a given data set organized as commented before, we implemented an algorithm that solve Eq.(6) to each data i $(1 < i < M)$ taking a given $\Delta[k]$ value. The algorithm takes an initial value β_0 and solve Eq.(6) to find $\beta_1[i]$, next it uses $\beta_1[i]$ to calculate $\beta_2[i]$, and so on. Despite the fast convergence, we have used 350 steps. The last step gives the value $\beta[i]$ and using all data we obtain a curve $\beta[i](\Delta[k])$, *i.e.*, a $\beta(T)$ curve to the given Δ value, where each $\beta[i]$ is calculated independently.

According to Eq.(4), Δ depends on the difference between T_M and T^{**}. For the data analyzed here, the interval adopted is: 0.102 K $\leq \Delta \leq$ 1.100 K. The algorithm starts with $\Delta[1] = 0.102$ K and using steps of 0.002 K it covers all this interval. At the end, the algorithm has a surface with 500 curves of $\beta(T)$, one for each Δ value. Now it is necessary to define a criterion to choose the curve that represents the correct behavior of β with the temperature.

2.4 β(T) Curves and the Choosing Criterion

To exemplify the use of our approach and the Δ choosing criterion, let us define a special data set. We take some typical parameters to Eq.(1) and calculate the corresponding values of S in a given temperature interval. Our hypothetical compound has the following characteristics: The temperatures of the NK and NI phase-transitions are, respectively, $T_{NK} = 300.00$ K and $T_{NI} = 320.00$ K. $S^{**} = 0.250000000$ u, $c_0 = 0.354653103$ u, $T^{**} = 320.100$ K and $\beta = 0.25$. Using these parameters we calculate $S(T)$ in the interval from $T_1 = 300.200$ K to $T_M = 319.800$ K taking steps of 0.100 K. At the end, the results obtained with our approach must reproduce these parameters. In our calculations we used 5 decimal places to represent the $S(T)$ values and 3 to the temperatures, that are typical values for birefringence data.

Figure 1 shows a set of $\beta(T)$ curves obtained with different values of Δ.

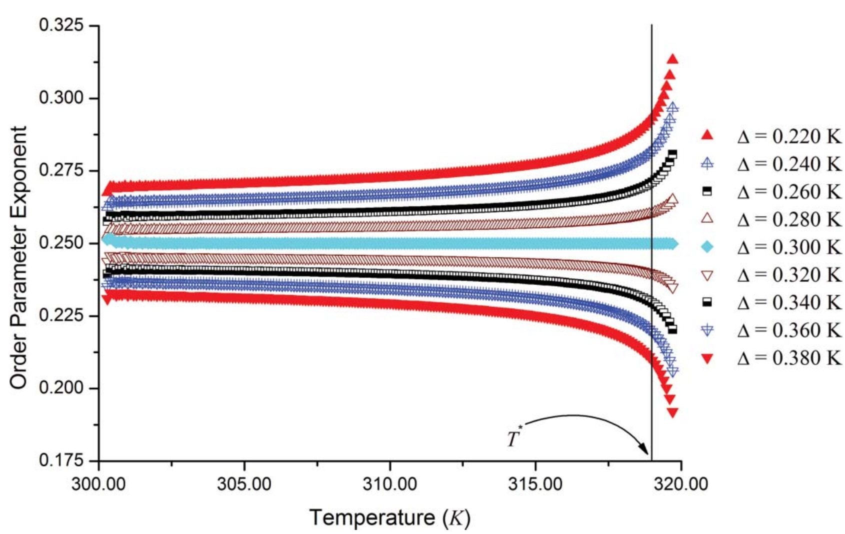

Figure 1. Split of the $\beta(T)$ curves for different values of Δ. Here we show the results obtained with a hypothetical data set. These curves present the following behavior: For $\Delta < 0.300$ K the $\beta(T)$ curves are concave, being the increasing with the temperature faster near the nematic to isotropic phase-transition region, $T_{NI} = 320.00$ K. If we have $\Delta > 0.300$ K the curves are convex and the decreasing is also faster near T_{NI}. The value $\Delta = 0.300$ K represents a transition between these two behaviors. The vertical line delimits the hypothetical NI phase-transition critical-like region.

From Fig. 1 one observes the following behavior of the $\beta(T)$ curves: When Δ is smaller than 0.300 K, the curves present a concavity and near to T_{NI} they increase more rapidly. On the other hand, when Δ is bigger than 0.300 K, the curves are convex and they decrease faster near T_{NI}. Therefore, the value $\Delta = 0.300$ K represent a transition between these two behaviors and the resulting curve presents a constant profile. Our choosing criterion considers the behavior expected to β at the NI phase-transition critical-like region.

The critical-like region is determined by the Landau-Ginzburg criterion [4,11]. According to the LCs literature [11], this region is defined by the interval: $T^* \leq T \leq T^{**}$—where T^* is the lowest temperature down to which one could supercool the isotropic phase. As it was shown by Mukherjee [1], $T_{NI} - T^*$ must be approximately equal to 1 K. Considering this information, one sees that at least 8 β points are within the critical-like region. In this region, the β values must be constant and the curve presenting this behavior is that one given by $\Delta = 0.300$ K. Synthesizing, our choosing criterion is: The value of Δ that furnishes the correct profile for $\beta(T)$ is the one which gives the expected β constant behavior in the critical-like region. The profiles of the $\beta(T)$ curves show clearly the convergence to this constant behavior [11]. According to this criterion, the results shown in Fig. 1 are in complete agreement with our expectations: $\beta(T) = 0.25$ and $\Delta = T^{**} - \mathrm{T}_1 = 0.300$ K.

2.5 *β*(T) *Curves and Errors*

Real experimental data ever have associated a random error. Our idea is to study the influence of these errors on the $\beta(T)$ curves or β values. According to Eq.(6), each β point is a multivariable function: $\beta = \beta(T, T_1, T_M, S, S_1, S_M, \Delta)$. From the propagation of uncertainty theory [12] we have:

$$\delta_\beta = \left[\left(\frac{\partial\beta}{\partial T}\right)^2 \delta T^2 + \left(\frac{\partial\beta}{\partial T_1}\right)^2 \delta T_1^2 + \left(\frac{\partial\beta}{\partial T_M}\right)^2 \delta T_M^2 + \left(\frac{\partial\beta}{\partial S}\right)^2 \delta S^2 + \ldots + \left(\frac{\partial\beta}{\partial \Delta}\right)^2 \delta \Delta^2 \right]^{1/2} \tag{7}$$

where δ represents the errors in the respective quantities.

We can calculate numerically these derivatives and by considering a hypothetical error to the quantities, we can estimate the errors of the β points. These calculations are made as follow: We consider the errors on the S values as being the typical resolution of birefringence measurements, 10^{-4} [9]. To the temperature measurements T, T_1, T_M and Δ, we consider errors of 0.01 K. We sum 1/20 of the error in T, for example, and run the program to calculate the corresponding $\beta(T + \delta T/20, \ldots, \Delta)$ curve, maintaining all others parameters fixed. At the sequence, we subtract 1/20 of the error and re-run the program obtaining the $\beta(T - \delta T/20, \ldots, \Delta)$. The difference between these curves divided by 1/10 of the error give the numerical value of the derivative. Repeating this process to each quantity we have all derivatives of Eq.(7) and, finally, the total δ_β error. Figs. 2 and 3 show the results obtained with the hypothetical data.

From Figs. 2 and 3 we see the influence of the experimental errors on the β points. These results show that we can expect big fluctuations near the ending points T_1 and T_M. The errors due to $T[i]$, T_1, $S[i]$ and S_1 give big contributions to δ_β at the region of T_1. At the T_M region, the errors due to T_1, $S[i]$ and S_1 are not so important, but the errors caused by $T[i]$ and T_M are. At T_1 region the errors due to T_M are negligible. The error caused by S_M is negligible for almost temperatures, but it shows a increasing at the T_M region. The error caused by Δ increases with the temperature, being this increasing faster near T_M.

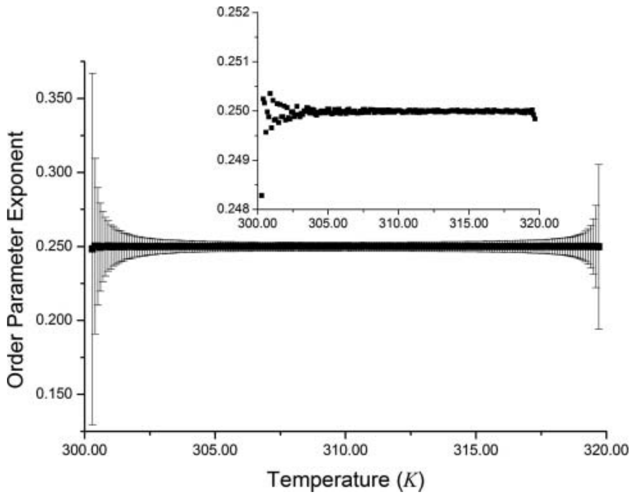

Figure 2. Propagation of the errors to the β points. From this result we note that near to the ending points T_1 and T_M the uncertainty on the measurements can cause big fluctuations of the β points. In fact, as we see in the minor graph, until the rounding errors are significant in these regions.

To finalize the analysis on the errors influence, we study the consequences of an eventual error on the ending points measurements. The calculations are made as follow: We sum the error on the measurement, T_1 for example, and rum the program to obtain the new $\beta(T)$ curve with the error in T_1. All other quantities were fixed. Then, we subtract the error and obtain other $\beta(T)$ curve. Repeating to the other parameters we have the result shown in Fig. 4.

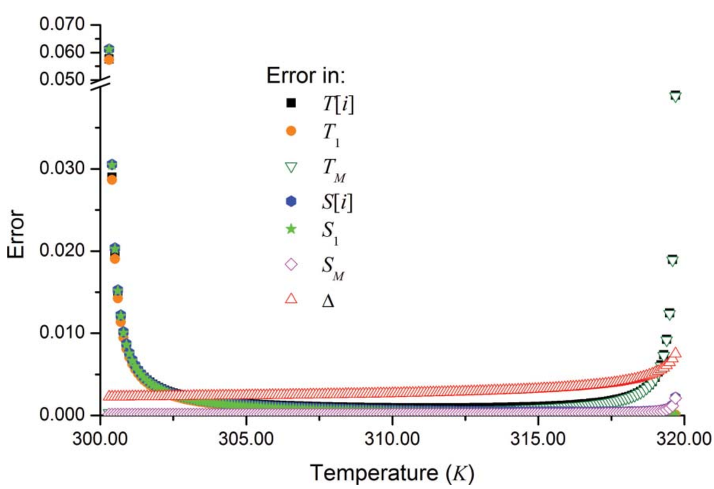

Figure 3. Detaching the errors caused by each physical quantity of Eq.(6). These are the contributions of each term of Eq.(7) to the errors bars shown in Fig. 2.

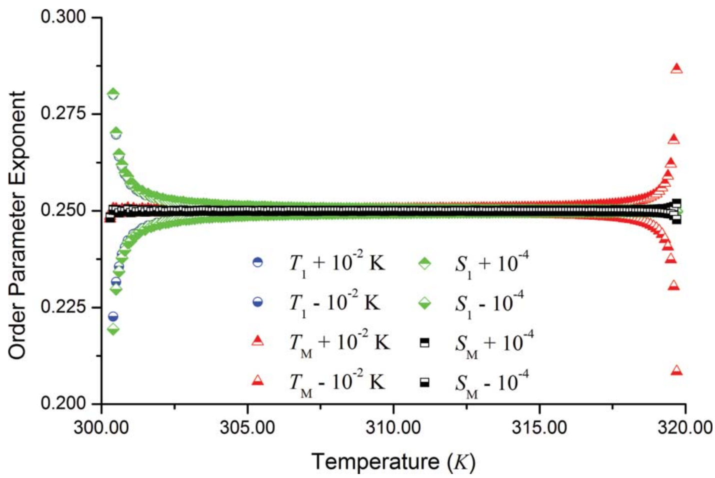

Figure 4. Analysis of the influence of the errors of the ending points measurements. One can note that these errors produce systematic deviations at these points. The errors on T_1 and S_1 give the same diverging behavior at the region of T_1: When we sum the error the $\beta(T)$ curve presents a concave diverging behavior; when we subtract, the curves present the opposite behavior. As it had been noted in Fig. 3, the error on S_M is negligible. The error on T_M produces a diverging behavior at its region; the curve increases if we sum the error, decreases if we subtract.

3. Experimental Data Analysis

3.1 Re-Analyzing the 6CB Δn *Experimental Data*

Recently, we analyzed the 6CB birefringence Δn experimental data measured by Chirtoc et al. [9]. Our analysis intended to show the constancy of β along the nematic phase [11]. Here we re-analyze these data considering the influence of the experimental errors.

The 6CB experimental data were measured in the interval $293.584 \leq \mathrm{T} \leq 301.084$ K, being $T_{NI} = 301.27$ K [9]. The extraordinary refraction index and temperature were measured with a resolution of 10^{-4} and 0.01 K, respectively. Here we adopt these resolutions as the experimental errors, which certainly underestimate the real values. The calculations are made as explained before and the results are shown in Figs. 5 and 6.

Results shown in Fig. 5 confirm our previous conclusion [11]; the order parameter exponent of 6CB is constant along the entire temperature interval in which the data were taken. Fig. 6 shows that in real data analysis the influence of the errors on the experimental quantities is more complex, but like observed in Fig. 3, the errors on the measurements may create big fluctuations at the ending points T_1 and T_M.

3.2 7CB Δn *Experimental Data*

Now we present the results obtained with the 7CB Δn experimental data, also measured by Chirtoc et al. [9]. Fig. 7 shows the split of the $\beta(T)$ curves for different values of Δ.

The first results obtained with the 7CB Δn data present some difficulties. Now we don't have a clear convergence at the critical region and we need to understand why. Studying the errors caused by each physical quantity and the influences of each one to the $\beta(T)$

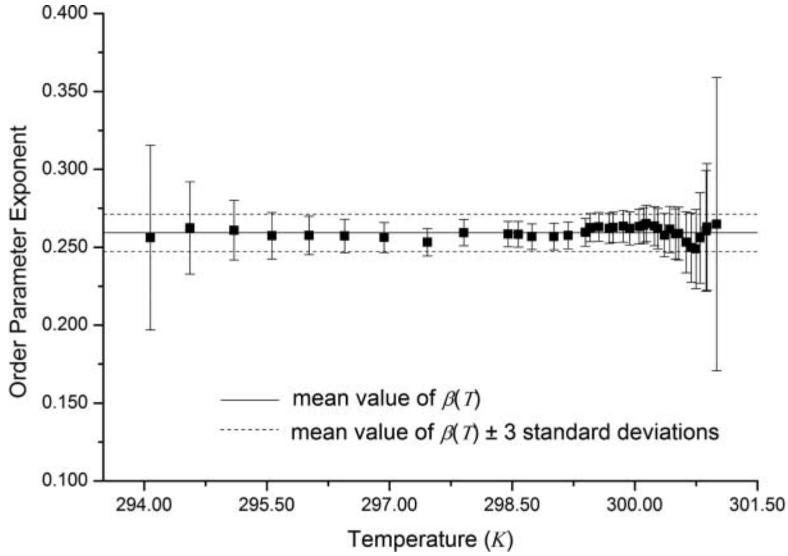

Figure 5. Re-analysis of the 6CB birefringence (βn) experimental data [9,11]. Now we consider the influence of the experimental errors on the β points. From these results, we observe that all β points are equal to mean value of the β(T) curve, $\bar{\beta} = 0.259$, confirming that β is constant along the entire interval which the data were taken.

curves, Fig. 4, we observed that a possible error on the T_M temperature may cause such behavior. Then we decided to re-analyze the data but now excluding the last measurement M. In Fig. 8 we show the result obtained considering the $M - 1$ measurement as the high temperature ending point.

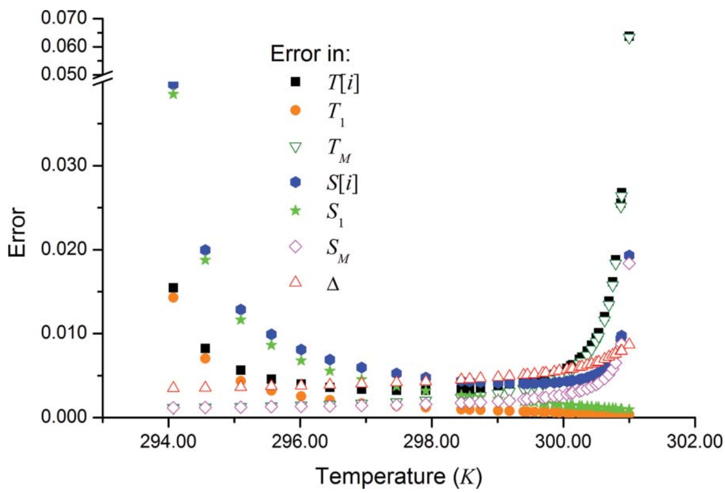

Figure 6. Here we have the contributions of each term of Eq.(7) to the errors bars shown in Fig. 5. These curves resemble the ones shown in Fig. 3, but the fluctuations on real experimental data present a more complex behavior and the influence of each quantity is more distinguishable.

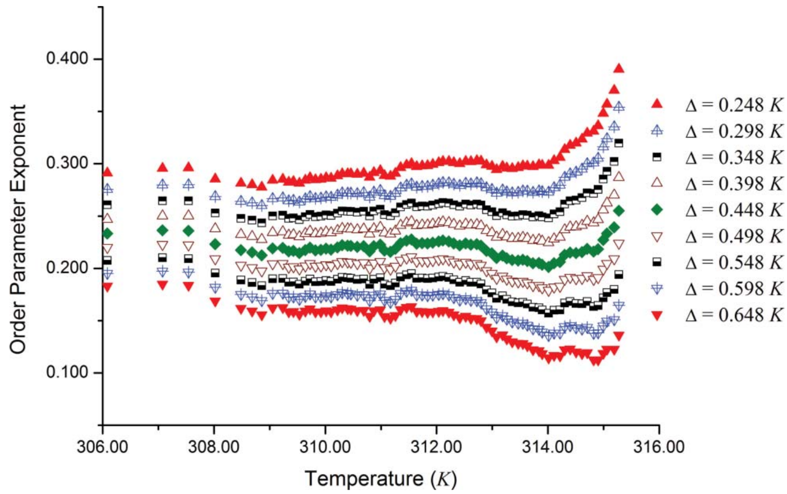

Figure 7. Split of the $\beta(T)$ curves for different Δ values for the 7CB Δn experimental data [9]. Different from the observed to 6CB Δn and 7CB anisotropy in the thermal conductivity (Δk) [11], the $\beta(T)$ curves obtained with the 7CB Δn data do not show a clear convergence to the constant behavior at the critical-like region; the data show a systematic increasing at this region.

The analysis of the 7CB Δn data shows that our approach is very sensible to the ending points measurements and that for some data sets the convergence at the critical-like region can be not clear. On the other hand, we see that a more accurate analysis of the experimental data can help us to surpass these eventual difficulties.

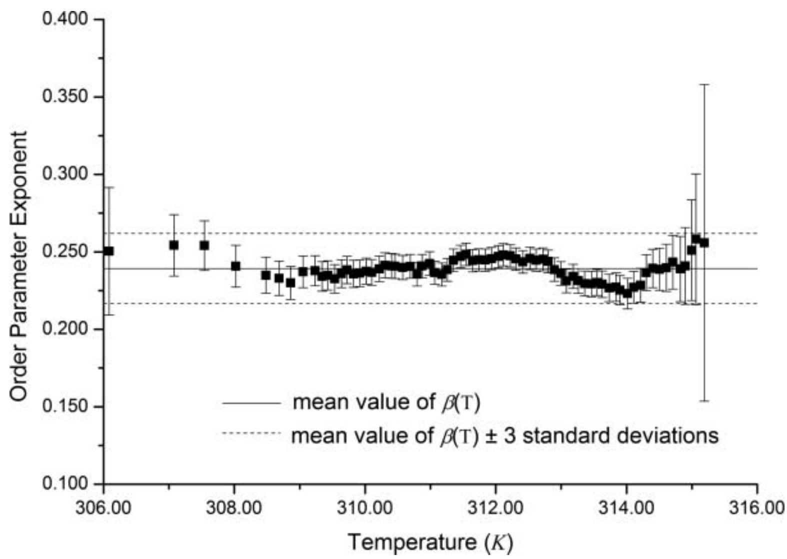

Figure 8. $\beta(T)$ curve obtained with the 7CB Δn experimental data [9]. Analyzing the experimental data we concluded that the convergence problem observed in Fig. 7 is caused by the temperature measurement T_M. Excluding this measurement we obtain this new $\beta(T)$ curve that agrees with that obtained with 6CB Δn and 7CB anisotropy in the thermal conductivity Δk [11].

4. Final Remarks and Conclusions

In this paper we presented a new approach to determine the β critical-like exponent of the NI phase-transition. Our approach reveal that this exponent presents a constant behavior along the entire range which the experimental data were taken and for the 7CB Δk data this conclusion is valid to the entire domain of the nematic phase [11].

Most critical problems in the analysis of β appear due to the large number of free fit parameters and the use of experimental data out of the critical-like region in the calculations. In our approach we reduced the number of free parameters and, how it makes an independent determination of β for each temperature point, we use the expected behavior of β in the critical-like region to choose the unique free parameter of the method; the value of Δ. We used hypothetical data to exemplify the use of the approach and show what kind of results we expect from it. We studied the influence of the experimental errors an their consequences on the $\beta(T)$ curves. The results obtained shows that the β points are very sensible to the experimental errors, being this sensibility bigger near to the ending points T_1 and T_M. Despite this sensibility, an accurate analysis of the influence of each quantity in the $\beta(T)$ curve can help us to refine the results obtained, as we observed in the 7CB Δn analysis.

Acknowledgments

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