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Corresponding states of order parameter in nematic liquid crystals

M. Simões and D. S. Simeão*

Departamento de Física, Universidade Estadual de Londrina, Campus Universitário, 86051-990 Londrina (PR), Brazil

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In this work, experimental data points from which the profile of the order parameter of nematic liquid crystals can be obtained, mainly magnetic susceptibility anisotropy and dielectric anisotropy, will be used to show that when rescaled they coalesce along a common line that extends from the nematic-isotropic phase transition region, until the nematic-crystalline phase transition region. A large set of experimental data of a diversity of nematic compounds that share the presence of a nematic-isotropic and a nematic-crystalline phase transition, without another phase within, has been collected from the liquid crystals literature. Taking for each of them the temperatures of these two phase transitions as fixed points, a common temperature scale has been constructed and, in this scale, the value of each physical quantity has been uniformly fixed at the nematic-crystalline phase transition temperature. This procedure has revealed the existence of a law of corresponding states that covers the entire nematic phase. As the values assumed by these physical quantities can be used to measure the macroscopic order parameter, the use of this temperature scale suggests that it presents a common behavior that covers the entire nematic phase.

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I. INTRODUCTION

Among the most fertile properties of the matter, the macroscopic anisotropy presented by some materials occupies a detached position. As a rule, it results from asymmetries at the molecular level whose macroscopic effects furnish a good guide to the comprehension of the microscopic structure of the matter [1]. Particularly surprising is that even in liquids macroscopic anisotropies can be found, the nematic liquid crystals (NLCs) being the simplest of these substances [2]. Their anisotropies cover a broad range of properties like viscosity, elasticity, birefringence, electric permittivity, and magnetic susceptibility, etc. Each of these properties is a function of the degree of alignment of the anisotropic grains that constitute the NLCs (molecules for thermotropics and micelles for lyotropics), this alignment being expressed by an order parameter S, which can be measured through the use of experimental data of these properties [2]. As the temperature interval at which the nematic phase is found is a particular characteristic of a given material, it is assumed that the profile of S along the nematic phase must be independently determined for each different liquid crystal compound. Consequently, along the years, for a large number of different compounds, the order parameter profile has been measured through the measurement of the anisotropy presented by these macroscopic properties. The aim of this paper is to show that, with the use of a simple linear rescaling, these measurements can coalesce along a unique line, suggesting that the thermal behavior of the order parameter presents a common profile that encompasses the entire nematic phase and therefore may not depend on the specific compound or physical property under study. To obtain these results, experimental data of some independent physical properties from which S is usually obtained, mainly the magnetic susceptibility anisotropy and dielectric anisotropy, have been collected from the liquid crystals literature and linearly rescale. As a result, the corresponding experimental points become distributed along a common curve. The simplicity of the rules leading to this result reveals that along the entire range of the nematic phase the molecular degree of alignment may present a universal temperature dependence.

A theoretical explanation to these results will not be afforded here. Nevertheless, some existing expressions [3–6] establishing a functional relationship between the order parameter and temperature will be used to produce a fit of the experimental data. In the next section the ideas that motivated this study, and the experimental results that illustrate it, are discussed and presented. In the ensuing section, some consequences of these achievements for the concept of macroscopic order parameter are discussed. At the conclusion, some questions that a theory explaining this universality must answer will be discussed.

II. NEMATIC TEMPERATURE SCALE

Here, experimental data of magnetic susceptibility anisotropy and dielectric anisotropy will be linearly rescaled. The connection between the following results and the order parameter profile will be discussed in the next section. As discussed by Gray [7], even small differences in the chemical structure of nematic molecules can provoke big differences in their phase diagram and respective transition temperatures; such properties are so singular that they are used to characterize a given material. These facts challenge us to find a way to compare the profile of a specified physical property in different compounds presenting the same sequence of phases. When the temperature is the running parameter, this procedure can be implemented by means of a twofold process; a rescaling that unformizes the temperature attributed to the common critical point and a regularization on the value of the physical property at such point [8,9]. Nevertheless,

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*Electronic address: simoes@uel.br

this procedure only permits a local comparison, a most valuable result would be obtained if it can be extended to the entire range of the phase. This could be accomplished if the same temperatures could be attributed to the equivalent transition points bordering a given phase, and a one to one correspondence could be made between all points of the interval, allowing a global comparison of the values assumed by the physical property. For some NLCs this idea can be easily implemented. Instead of a unique critical point, some of them present two fixed points, one at the nematic-isotropic phase transition (*NI*) and another at the nematic-crystalline phase transition (*NC*) point. The existences of two transition temperatures permit the collective establishment of two fixed points and, as consequence, the definition of a new temperature scale; the nematic scale [10,11]. That is, for compounds for which the nematic temperature scale can be defined, the physical states will not characterize a particular compound, but through a global correspondence of states, they could join in a unique and universal line, expressing the uniqueness of the thermal behavior of the nematic phase [3,4].

To give experimental support to such reasoning, it will be applied here to two different standard physical properties whose experimental data are abundant in the liquid crystals literature; the magnetic susceptibility anisotropy ($\Delta\chi$) and the dielectric anisotropy ($\Delta\epsilon$) [2]. For the compounds listed in the Appendix, a uniformized temperature scale was constructed in such a way that for the *NC* it was attributed the temperature $t=0$, while for the *NI* it was attributed the temperature $t=1$. That is, if T_{NI} is the Kelvin temperature of the *NI* and T_{NC} is the Kelvin temperature of the *NC*, then the nematic temperature t is related with the Kelvin temperature T by the relation

$$t=\frac{T-T_{NC}}{T_{NI}-T_{NC}}. \tag{1}$$

Afterwards, the profiles of experimental data of $\Delta\chi$ and $\Delta\epsilon$ have been uniformly regularized in such a way that they assume the value 1 at the *NC* phase transition. Figures 1 and 2, show the result of the application of the procedure described above. In the Appendix, Tables I–III showing the scientific names, abbreviations, phase transitions temperatures, and the references from where these data have been taken are presented. As guessed, the use of a unique temperature scale makes the diversity found in the experimental data disappear; they have joined in a single curve. The internal agreement obtained with linear rescalings demonstrates that, when regularized and expressed by means of the nematic temperature scale, each of these physical properties lost its individuality and a common behavior that encompasses the entire range of the nematic phase is observed.

It is important to distinguish the universality that we have found from that usually found on critical phenomena. Critical phenomena universalities arise from the scale invariance observed at very narrow regions, bordering critical points, where large fluctuations connecting neighbor phases dominate the scenario. They are described by the renormalization group theory [12,13], which, surely, cannot be responsible for the global regularities that we have found. Therefore the data agglutination observed on the figures is a sign that the use of the nematic temperature scale has reveled that for all compounds of each figure the same underlying physical behavior is under action; when rescaled, the thermal profile of the order parameter becomes the same.

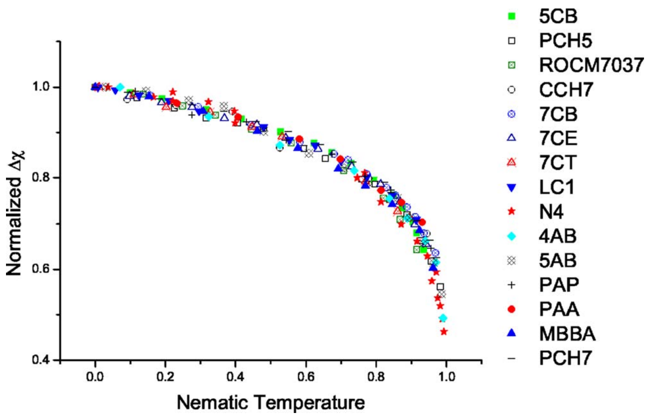

FIG. 1. (Color online) Normalized experimental data of the magnetic susceptibility anisotropy expressed in terms of the nematic scale of temperature. The points have been homogeneously rescaled to assume the value 1 at the temperature $t=0$, which corresponds to the nematic-crystalline phase transition point. The temperature $t=1$ corresponds to the nematic-isotropic phase transition point. The profile acquired by the rescaled points shows that they join together in a unique and universal line. The complete name of the compounds and the references from where the data points have been obtained are given in the Appendix.

III. ORDER PARAMETER PROFILE

Above, it has been shown that with the use of our rescaling process, in compounds having a nematic-isotropic and a nematic-crystalline phase transition, without another phase within, the experimental data of two of these physical properties have coalesced along two common curves, each one

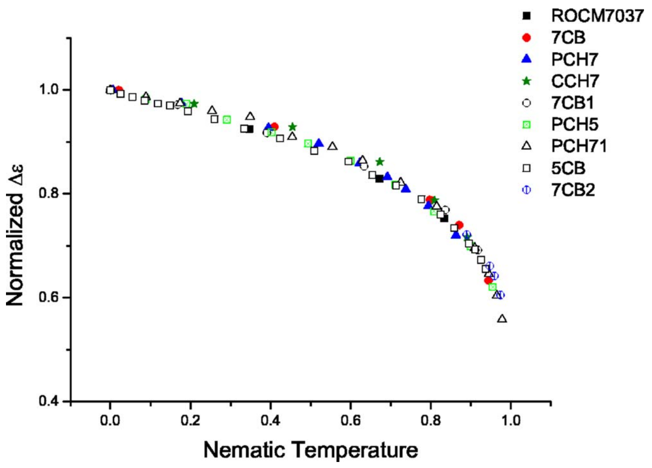

FIG. 2. (Color online) Normalized experimental data points of the dielectric anisotropy expressed in terms of the nematic scale of temperature. The rescaling is the same done in Fig. 1. Again, the data points merge to a unique line.

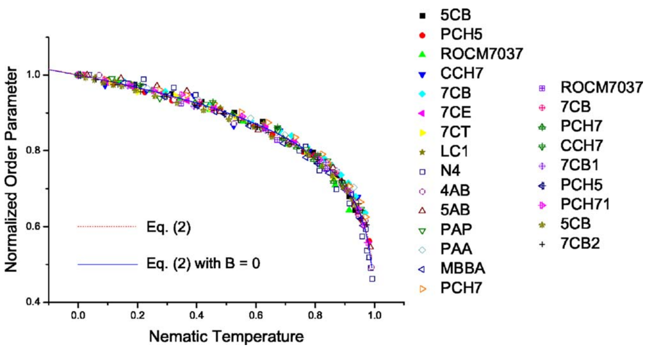

FIG. 3. (Color online) In this figure a union of Figs. 1 and 2 is presented. This figure expresses the main result of this work; the profile acquired by these superposed points show that they coalesce in a unique and universal line that is the same for all physical properties and compounds listed in the Appendix. Only a universality on the rescaled order parameter profile could be responsible for such behavior.

characterizing a different property. Nevertheless, as the order parameter is proportional to $\Delta\chi$ and approximately proportional to $\Delta\epsilon$ [2], there is also another universality that must be shared by these two curves. When the data points of these figures are superposed, as shown in Fig. 3, it is observed that the line of coalescence of both figures is again the same for all physical properties and compounds listed in the Appendix. The reason of this agglutination of experimental data can be easily guessed: the rescaling that we have used reveled that the order parameter presents a common profile along the entire range of the nematic phase. This is the main result of this work.

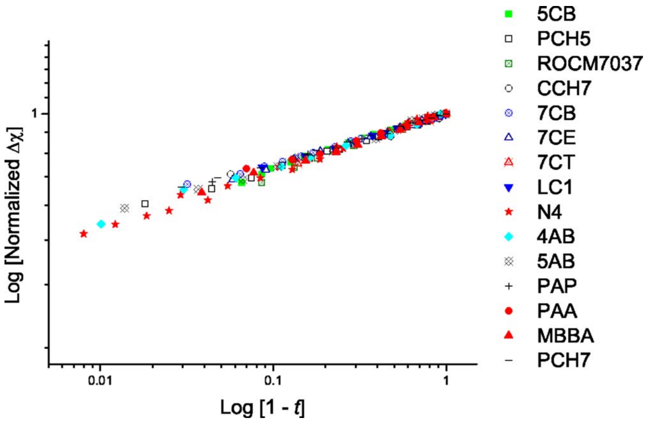

FIG. 4. (Color online) A log-log graph of the experimental data of the magnetic susceptibility anisotropy, shown in Fig. 1. With this parametrization the experimental data become ordered along a straight line.

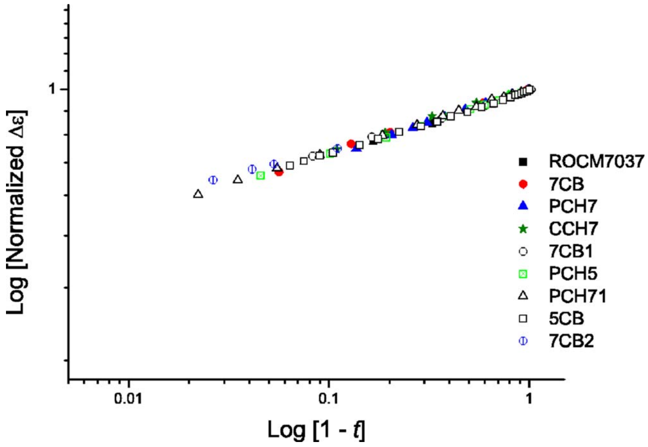

FIG. 5. (Color online) A log-log graph of the experimental data of the dielectric anisotropy, shown in Fig. 2. As in Fig. 3, the adopted parametrization makes the experimental data become ordered along a straight line.

In order to get a glimpse of the kind of curve to which these points converge, a log-log graph of the data shown in Figs. 1 and 2 has been displayed in Figs. 4 and 5. Although only a detailed study can determine the exact form of this curve, the profile assumed by the data points is enough uniform to state that a power law behavior dominates its form. Indeed, there are in the liquid crystals literature some propositions describing the analytical expressions to the order parameter that are consistent with the profile observed in these figures [3,4,6]. The Maier-Saupe [3] approach is the cornerstone of all them, the Haller expression being widespread used in fits of individual order parameter profiles [4]. Recently, Chirtok *et al.* [6] have proposed a generalization of the Haller approach that, according to the authors, can improve the known results for the critical exponent β_c of the nematic-isotropic phase transition. Their expression is given by

$$P = A\left[B + (1-B)\left(1 - \frac{T}{T^*}\right)^{\beta}\right], \tag{2}$$

where P is the physical property under consideration and A, B, β, and T^* are parameters to be determined by the experimental data. Using this expression to fit the data exposed in Fig. 3, it is found that

$$A = 1.002 \pm 0.002, \quad B = 0.2 \pm 0.1, \quad T^* = 1.000 \pm 0.003,$$

$$\beta = 0.21 \pm 0.02.$$

Otherwise, when the Haller expression ($B=0$ in the above equation) is used to fit the data it is found that

$$A = 1.002 \pm 0.001, \quad T^* = 1.016 \pm 0.006,$$

$$\beta = 0.159 \pm 0.003.$$

In order to interpret these results correctly and allow comparisons with those published in the current literature we will make here some observations about the uncertainties that accompany them. The uncertainties in the above data correspond to the standard error, which points to the uncertainty associated with the mean value of the random variable with relation to the unknown real value. As we have considered a large number of experiments to obtain the mean values of the above parameters, the standard error attributed to them must decrease to be in accord with the idea that when the number of experiments becomes infinitely large the error of the mean must go to zero. This concept is different from the standard deviation, which gives the interval in which a measurement of this variable is hoped to be found. For example, to the parameter β of the Haller approach, the calculus of the standard deviation has given $\sigma=0.013$, clearly larger than the standard error, indicating that the values found to β in the liquid crystals literature are in agreement with our results. We also would like to observe the difference found for the exponent β in the two expressions considered above. Such sensibility of β to the form of the curve used to make a fit of the experimental data points has been observed by Chirtok *et al.* [6], in a paper in which a secure way to determine the universality class of the critical exponent β_c that would characterize the nematic-isotropic phase transition is looked for. Following such reasoning, it must be emphasized that the experimental data used in this work do not allow an evaluation of such β_c. The data that we have used encompass the entire nematic phase, and β_c characterize the behavior of the order parameter only at the neighborhoods of the nematic-isotropic phase transition region, this is the reason why we have called our parameter β and not β_c. So, for the purposes of this work, β is only a fitting parameter that measures the uniformity of the experimental data. Consequently, a theoretical interpretation of the nature and meaning of the universality found in Fig. 3 must be addressed before a physical interpretation of the fitting parameters used in any guessed curve can be made.

Finally, as the order parameter can be measured by using different techniques or/and physical properties, a comparative study of these different procedures for a some compound has been also done. Such a study has been done with the experimental data of PAA (4-4′-azoxydianisole) and the results are shown in Fig. 6. The references used to obtain the experimental data are displayed in Table III of the Appendix. Details about the techniques and physical properties corresponding to each measurement can be found in the quoted references. All data have been submitted to the rescaling defined above, and the dashed line corresponds to the curve ($B=0$) of Fig. 3. Essentially, the data displayed in this graph confirms the idea that the order parameter presents a universal profile that appears to collapse to the neighborhoods of the same curve. However, the quality of the agreement between these different experimental data seems to become poor as the *NI* transition is approached. Nevertheless, as long as the fluctuations associated with each one of these measurements is considered, it is concluded that the disagreement may not be as high as it appears. In fact, the highest disagreement is observed with the electron spin resonance (ESR) data. Nevertheless, as explicitly pointed by the authors of the measurements [14], two factors could introduce errors on their measurements; they have not checked the accuracy of their temperature settings and, furthermore, in their measurements the PAA compound was not completely purified. These factors may be responsible for the deviations observed around the *NI* transition. In our calculations we have observed, for example, that a small shift in the temperature values could make their data collapse to the mean curve. Another set of measurements that deserves consideration is the one corresponding to nuclear magnetic resonance at constant molar volume (NMR-CMV) [15]. These data are taken at constant volume, leading to a pressure variation between 1 bar at the *NC* phase, and 640 bars at the *NI* phase. This pressure change has led to a shift in the *NI* temperature of around 30 °C. Nevertheless, even with so high variation in the thermodynamical conditions, the profile of the rescaled curve has not presented any appreciable change. By itself this is an interesting result, which strongly confirms the hypotheses that the order parameter presents a universal profile when expressed through the nematic temperature scale.

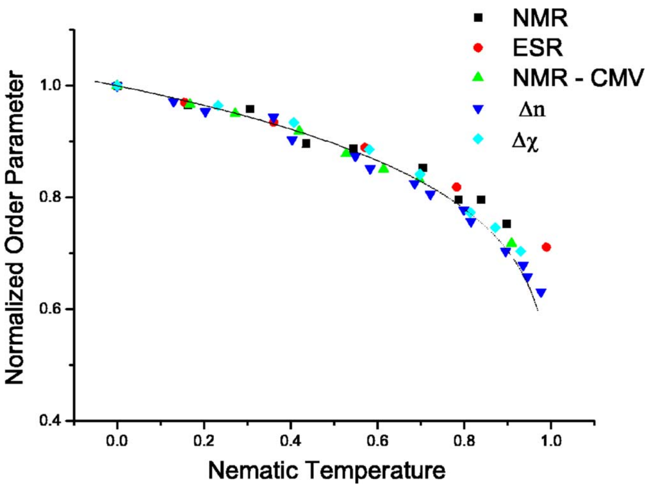

FIG. 6. (Color online) Normalized experimental data points of physical properties from which the order parameter of the PAA can be obtained. The physical properties correspond to nuclear magnetic resonance (NMR), electron spin resonance (ESR), nuclear magnetic resonance at constant volume (NMR- CMV), birefringence (Δn), and anisotropy of the magnetic susceptibility ($\Delta\chi$). The rescaling is the same done in Fig. 1 and the corresponding points are indicated in the figure by the above abbreviations. Except for the neighborhoods of the *NI* the data points seems to merge with the neighborhoods of a unique line. The largest deviation is observed for the ESP data and, as commented on in the text of the paper and recognized by the authors of the measurements, is probably associated with experimental errors, like inaccuracy on temperature measurements.

IV. CONCLUSION

In this work, rescaled experimental data points of some physical properties from where the profile of the order parameter of NLCs can be derived have been studied. All compounds present a nematic-isotropic and nematic crystalline phase transition, without any other phase within and, through the use of a compound dependent temperature scale, these experimental data points have been normalized at the *NC* phase-transition temperature, revealing a unique coalescence curve dominated by a well defined power law behavior along the entire range of the nematic phase. As these properties are or proportional ($\Delta\chi$) or approximately proportional to the order parameter, the uniqueness of their coalescence curve suggests that the order parameter presents a universal behavior along the entire range of the nematic phase. The analysis presented in this work only permits us to take this as a very tempting hypothesis. A secure experimental conclusion only could be addressed when at least two conditions have been considered: an ample number of physical properties, from where the order parameter can be deduced, must be studied, and all approximations and assumptions involved in each one of them have been taken in account. Nevertheless, even being true that a universal behavior of the order parameter is a too strong conclusion in view of the fact that we have considered only few physical properties, the set of experimental data that we have considered is sufficiently incisive and ample to support further investigations in the universality that it definitively suggests.

Anyway, some of the known theories proposing a temperature behavior for the order parameter have been used to produce a fit of these points. Even producing fits with good quality, these theories cannot explain the physical origin of the universality found in the experimental data. As the universality exposed here encompasses the entire nematic phase, a theory explaining this universality must explain, for example, why the order parameter behavior remains uniform at the neighborhoods of the nematic-crystalline region. The observation of such behavior is a signal, for example, that a correlation between the degree of orientation and its center of mass position must exist at this region and, furthermore, save for the scaling that we have used, such correlation must be the same for all compounds, and encompass the entire nematic phase, including the nematic-isotropic phase transition region. Therefore the key to understand the universality that we have found stays in the elucidation of the physical meaning of the temperature scale that we have used, the nematic temperature scale. This temperature scale gives equal emphasis to all points of the nematic phase, including the neighborhoods of the two phase transition regions. As a global homogeneous behavior has been found, it suggests that to understand these results a theory considering simultaneously these two phase transitions must be proposed. As far as we know, a theory comprising the entire nematic phase, with these two phase transitions included, does not exist. This is the difficulty that a theory would overcome to give an explanation to our findings.

Finally, we would like to mention that the experimental data that we have used are restricted to the uniaxial order parameter only because the experimental data for this case is abundant in literature, so abundant that the number of compounds where such universality is found is so large that, even being an experimental result, we believe that the proposed universality is convincing. Furthermore, the possibility that this same kind of universality could be also shared by other physical properties, the biaxial case included, is so stimulating an issue that, surely, it must be the subject of future investigation.

ACKNOWLEDGMENTS

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APPENDIX

TABLE I. Compounds and references of the experimental data presented in Fig. 1.

Abbreviation	Scientific name	T_{NC} (°C)	T_{NI} (°C)	References
5CB	4-n-pentyl-4′-cyanobiphenyl	24	35.3	[16,17]
PCH5	4-cyano-4′-n-pentyl-cyclohexanephenyl	30	55	[16,18]
ROCM7037	4-(5-n-heptyl-pyrimidin-2-yl)-benzonitrile	45	51	[16,19]
CCH7	4′-n-heptyl-bicyclohexyl-4-carbonitrile	71	83	[16,20]
7CB	4-n-heptyl-4′-cyanobiphenyl	28.5	42	[16,21]
7CE	4-n-heptyl-benzoic acid 4-cyano-phenyl	44	56.5	[16,22]
7CT	4-n-heptyl-4′-cyanotolane	58.5	67.5	[16,23]
LC1	4-n-heptyl-thiobenzoic acid S-(4-cyano-phenyl) ester	82	92.4	[16,24]
N4	4-methoxy-4′-n-butylazoxybenzene (mix of two comp.)	17.9	74.9	[25,16]
4AB	4-4′-di-n-butylazoxybenzene	22	71.9	[25,26]
5AB	4-4′-di-n-pentylazoxybenzene	24	67.6	[25,26]
PAP	4-4′-di-ethoxyazoxybenzene	136.8	168.4	[25,27]
PAA	4-4′-azoxydianisole	118	135.2	[28]
MBBA	4-methoxybenzylidene-4′-n-butylaniline	19	45	[28]
PCH7	4-cyano-4′-n-pentyl-cyclohexanephenyl	30	57.3	[29,30]

TABLE II. Compounds and references of the experimental data presented in Fig. 2.

Abbreviation	Scientific name	T_{NC} (°C)	T_{NI}	References
ROCM7037	5-n-heptyl-2-(4′-cyanophenyl)-pyrimidine	45	51	[19,31]
7CB	4-n-heptyl-4′-cyanobiphenyl	29.7	42.7	[23,31]
PCH7	4-cyano-4′-n-heptyl-cyclohexanephenyl	30	59	[31,32]
CCH7	4-n-heptyl-bicyclohexyl-4′-carbonitrile	71	84.1	[20,31]
7CB1	4-n-heptyl-4′-cyanobiphenyl	30	42	[23,33]
PCH5	4-cyano-4′-n-pentyl-cyclohexanephenyl	30	54.4	[18,33]
PCH71	4-cyano-4′-n-heptyl-cyclohexanephenyl	30	57	[32,33]
5CB	4-n-pentyl-4′-cyanobiphenyl	24	35.3	[23,34]
7CB2	4-n-heptyl-4′-cyanobiphenyl	30	42.1	[17,34]

TABLE III. Different experimental techniques used in the determination of the profile of the order parameter of the PAA (4-4′-azoxydianisole) compound. It is also shown the temperatures of the critical points, and the references from where the data points have been collected.

Technique	Abbreviation	T_{NC} (°C)	T_{NI} (°C)	References
Nuclear magnetic resonance	NMR	117	135	[35]
Electron spin resonance	ESR	117	136,2	[14]
Nuclear magnetic resonance at constant volume	NMR-CMV	117	164,4	[15]
Birefringence	Δn	117	135	[28,36]
Anisotropy of the magnetic susceptibility	Δ_χ	118	135,2	[28]

[1] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, London, 1959).

[2] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals 2nd Edition* (Clarendon Press, Oxford, 1993).

[3] W. Maier and A. Saupe, Z. Naturforsch. A **14**, 882 (1959).

[4] I. Haller, Prog. Solid State Chem. **10**, 103 (1975).

[5] C. Zannoni, *The Molecular Physics of Liquid Crystals* (Academic Press, London, 1979), Chap. 3.

[6] I. Chirtoc, M. Chirtoc, C. Glorieux, and J. Thoen, Liq. Cryst. **31**, 229 (2004).

[7] G. W. Gray, *The Molecular Physics of Liquid Crystals* (Academic Press, London, 1979), Chap. 1.

[8] H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Claredon Press, Oxford, 1971).

[9] E. A. Guggenhein, J. Chem. Phys. **13**, 253 (1945).

[10] M. Simões and S. M. Domiciano, Phys. Rev. E **66**, 061703 (2002).

[11] M. Simões and S. M. Domiciano, Phys. Rev. E **68**, 011705 (2003).

[12] K. G. Wilson, Rev. Mod. Phys. **55**, 583 (1983).

[13] M. E. Fisher, Rev. Mod. Phys. **46**, 597 (1974).

[14] S. H. Glarum and J. H. Marshall, J. Chem. Phys. **44**, 2884 (1966).

[15] J. R. McColl and C. S. Shih, Phys. Rev. Lett. **29**, 85 (1972).

[16] A. Buka and W. H. de Jeu, J. Phys. (France) **43**, 361 (1982).

[17] S.-T. Wu and C.-S. Wu, Phys. Rev. A **42**, 2219 (1990).

[18] T. Szczucinski and R. Dabrowski, Mol. Cryst. Liq. Cryst. **88**, 55 (1982).

[19] A. Boller, M. Cereghetti, M. Schadt, and H. Scherrer, Mol. Cryst. Liq. Cryst. **42**, 215 (1977).

[20] R. Eidenschink, D. Erdmann, J. Krause, and L. Pohl, Angew. Chem. **90**, 133 (1978).

[21] P. P. Karat and N. V. Madhusudana, Mol. Cryst. Liq. Cryst. **36**, 51 (1976).

[22] L. A. Karamysheva, E. I. Kovshev, and M. I. Barnik, Mol. Cryst. Liq. Cryst. **37**, 29 (1976).

[23] W. W. Beens and W. H. de Jeu, J. Chem. Phys. **82**, 3841 (1985).

[24] J. Krause and L. Pohl, Ger. Patent No. DE 2.603.293 (1977/08/11).

[25] W. H. de Jeu and A. P. Claassen, J. Chem. Phys. **68**, 102 (1978).

[26] J. van der Veen, W. H. de Jeu, M. W. M. Wanninkhof, and C. A. M. Tienhoven, J. Chem. Phys. **77**, 2153 (1973).

[27] M. E. Neubert, P. Norton, and D. L. Fishel, Mol. Cryst. Liq. Cryst. **31**, 253 (1975).

[28] W. H. de Jeu, W. A. P. Claassen, and A. M. J. Spruijt, Mol. Cryst. Liq. Cryst. **37**, 269 (1976).

[29] Hp. Schad, G. Baur, and G. Meier, J. Chem. Phys. **70**, 2770 (1979).
[30] L. Pohl, R. Eidenschink, J. Krause, and D. Erdmann, Phys. Lett. **60A**, 421 (1977).
[31] Hp. Schad and M. A. Osman, J. Chem. Phys. **75**, 880 (1981).
[32] L. Pohl, R. Eidenschink, J. Krause, and D. Erdmann, Phys. Lett. **60A**, 421 (1977).
[33] Hp. Schad, G. Baur, and G. Meier, J. Chem. Phys. **71**, 3174 (1979).
[34] B. R. Ratna and R. Shashidhar, Pramana **6**, 278 (1976).
[35] J. C. Rowell, W. D. Phillips, L. R. Melby, and M. Panar, J. Chem. Phys. **43**, 3442 (1965).
[36] W. H. de Jeu and P. Bordewijk, J. Chem. Phys. **68**, 109 (1978).